FUEL CELL POWER GENERATING PLANT AND ITS START/STOP OPERATION METHOD

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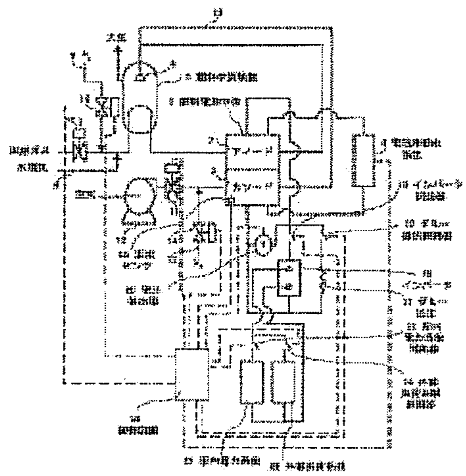
Abstract of **JP 11067254 (A)**

PROBLEM TO BE SOLVED: To provide a fuel cell power generating plant and its start/stop operation method capable of preventing the deterioration of a catalyst in starting operation or stopping operation and stably keeping cell characteristics without any drop. SOLUTION: An inverter 16, a dummy resistance 17, and a voltage detector 20 are connected in parallel to between an anode 2 and a cathode 3 through an inverter switch 18 and a dummy resistance switch 19. An in-house power line 21 and an outside load line 22 are connected in parallel to an AC output line of the inverter 16 so as to be switched through an in-house power line switch 23 and an outside load line switch 24. A temperature sensor 25 for measuring temperature is arranged in a hot spot in a stacked unit cell of a fuel cell body 1. A cell cooling water line 4, various kinds of valves and switches are controlled with a control device 26.



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CLAIMS

[Claim(s)]
[Claim 1]A fuel cell body which carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, A cell cooling system which controls temperature of a fuel cell body, and an inverter unit connected to an outgoing end of a fuel cell body, In a start/stop operation method of a fuel-cell-power-generation plant provided with an external load system switch which connects an external load system with this inverter unit, By supplying an output of said fuel cell body only to electric power system of a fuel-cell-power-generation plant within a station at the time of one at the time of start manipulation of a fuel-cell-power-generation plant, and stopping operation of operations, while making said external load system switch into an opened state. A start/stop operation method of a fuel-cell-power-generation plant provided with a step which carries out idle mode operation operated by the minimum load equivalent to load of only electric power system within a station.
[Claim 2]A step which controls generating load based on a stop command, and is reduced to said minimum load at the time of stopping operation of a fuel-cell-power-generation plant, A step which opens said external load system switch wide, and carries out said idle mode operation after said minimum load attainment, A step which controls said cell cooling system and carries out temperature fall operation of said fuel cell body in parallel to a step which carries out said idle mode operation, When said fuel cell body temperature lowers the temperature to idle mode shutdown temperature set up lower than operating temperature, Are parallel with a step which suspends said idle mode operation, and a step which suspends said idle mode operation, Have a step which carries out inert-gas-replacement operation and main part stopping operation including residual voltage control operation, and said inert-gas-replacement operation, It is operation of supplying inactive gas to a fuel cell body, and driving out residual gas at the same time it intercepts supply of reforming fuel from said fuel reformer and said oxidizer feed unit to said fuel cell body, and an oxidizer.
A start/stop operation method of the fuel-cell-power-generation plant according to claim 1, wherein said residual voltage control operation is operation which controls residual voltage by supplying a dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole.

[Claim 3]A start/stop operation method of the fuel-cell-power-generation plant according to claim 2 being temperature when said idle mode shutdown temperature reaches a range whose maximum temperature inside said fuel cell body is 150-180 **.
[Claim 4]In a step to carry out, temperature fall operation of said fuel cell body A cell temperature falling speed under said idle mode operation, And a start/stop operation method of the fuel-cell-power-generation plant according to claim 2 characterized by controlling said cell cooling system so that a cell temperature falling speed of a to [from said main part stopping operation after idle mode operation / a cell storage temperature] may be maintained [h] in 50 ** /or less.
[Claim 5]A step which controls said cell cooling system based on a starting command, and

carries out warming operation of said fuel cell body at the time of start manipulation of a fuel-cell-power-generation plant, When said fuel cell body temperature carries out temperature up to idle mode start-up temperature set up lower than operating temperature, A step which supplies reforming fuel and an oxidizer from said reformer and said oxidizer feed unit to said fuel cell body, respectively, and carries out said idle mode operation, and when said fuel cell body temperature reaches operating temperature, A start/stop operation method of the fuel-cell-power-generation plant [provided with a step which carries out external start manipulation which throws in said external load system switch and outputs electric power to said external load system] according to claim 1.
[Claim 6]A start manipulation method of the fuel-cell-power-generation plant according to claim 5, wherein said idle mode start-up temperature is the temperature of not less than 150 **.
[Claim 7]In a step which carries out warming operation of said fuel cell body, so that a cell heating rate from a cell storage temperature to just before said idle mode operation and a cell heating rate under idle mode operation may be maintained [h] in 50 ** /or less, A start/stop operation method of the fuel-cell-power-generation plant according to claim 5 controlling said cell cooling system.
[Claim 8]In a step which carries out warming operation of said fuel cell body, before fuel cell body temperature reaches 100 **, inactive gas containing 4% or less of hydrogen [a small amount of] is supplied to a fuel electrode of a fuel cell body, A start/stop operation method of the fuel-cell-power-generation plant according to claim 5 controlling residual voltage by supplying a dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole when cell voltage of said fuel cell body reaches more than voltage control starting potential set up beforehand.
[Claim 9]A fuel cell body which carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole.
A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively.
A cell cooling system which controls temperature of a fuel cell body.
An inverter unit connected to an outgoing end of a fuel cell body.
An external load system switch which connects an external load system with this inverter unit.
It is the stopping operation method of a fuel-cell-power-generation plant provided with the above, and said inactive gas of said fuel cell body supplied to either a fuel electrode or an oxidizing agent pole at least contains 0.1% or less of oxygen [a small amount of].

[Claim 10]A stopping operation method of the fuel-cell-power-generation plant according to claim 9 that an oxygen density in said inactive gas is characterized by being 0.005 to 0.05%.
[Claim 11]A fuel cell body which carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole.
A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively.
A cell cooling system which controls temperature of a fuel cell body.
An inverter unit connected to an outgoing end of a fuel cell body.
An external load system switch which connects an external load system with this inverter unit.
Are the fuel-cell-power-generation plant provided with the above, have a control means which controls said external load system switch, and by said control means. Idle mode operation operated by the minimum load equivalent to load of only electric power system within a station consisted of supplying an output of said fuel cell body only to electric power system of a fuel-cell-power-generation plant within a station, while making said external load system switch into an opened state feasible.

[Claim 12]An inert gas feeder which supplies inactive gas to said fuel cell body is formed, and. It is provided by dummy resistor connectable between a fuel electrode of said fuel cell body, and an oxidizing agent pole, and said control means, Based on a stop command, control generating load, and it is made to decrease to said minimum load at the time of stopping operation of a fuel-

cell-power-generation plant, At the same time it opens said external load system switch wide and carries out said idle mode operation after said minimum load attainment, When said cell cooling system is controlled, temperature fall operation of said fuel cell body is carried out and said fuel cell body temperature lowers the temperature to idle mode shutdown temperature set up lower than operating temperature, Suspend said idle mode operation, are constituted so that inert-gas-replacement operation and main part stopping operation including residual voltage control operation may be carried out, and said inert-gas-replacement operation, Are operation of supplying inactive gas to a fuel cell body from said inert gas feeder, and driving out residual gas at the same time it intercepts supply of reforming fuel from said fuel reformer and said oxidizer feed unit to said fuel cell body, and an oxidizer, and said residual voltage control operation, The fuel-cell-power-generation plant according to claim 12 being the operation which controls residual voltage by supplying said dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole.

[Claim 13]At the time of start manipulation of a fuel-cell-power-generation plant, said control means controls said cell cooling system based on a starting command, and carries out warming operation of said fuel cell body, When said fuel cell body temperature carries out temperature up to idle mode start-up temperature set up lower than operating temperature, When reforming fuel and an oxidizer are supplied from said reformer and said oxidizer feed unit to said fuel cell body, respectively, said idle mode operation is carried out and said fuel cell body temperature reaches operating temperature, The fuel-cell-power-generation plant according to claim 11 constituting so that external start manipulation which throws in said external load system switch and outputs electric power to said external load system may be carried out.

[Claim 14]A minute amount hydrogen containing gas feed unit which supplies inactive gas which contains 4% or less of hydrogen [a small amount of] in a fuel electrode of said fuel cell body is formed, and. It is provided by dummy resistor connectable between a fuel electrode of said fuel cell body, and an oxidizing agent pole, and said control means, At the time of said warming operation of said fuel cell body at the time of said start manipulation of said fuel-cell-power-generation plant, to timing before fuel cell body temperature reaches 100 **. When inactive gas which contains said a small amount of hydrogen from said minute amount hydrogen containing gas feed unit is supplied to a fuel electrode of a fuel cell body and cell voltage of said fuel cell body reaches more than voltage control starting potential set up beforehand, The fuel-cell-power-generation plant according to claim 13 controlling residual voltage by supplying said dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole.

[Claim 15]In a fuel-cell-power-generation plant characterized by comprising the following constituted so that main part stopping operation might be carried out, A fuel-cell-power-generation plant, wherein said inactive gas of said fuel cell body supplied to either a fuel electrode or an oxidizing agent pole at least contains 0.1% or less of oxygen [a small amount of] from said inert gas feeder.

A fuel cell body which carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole.

A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively.

An inert gas feeder which supplies inactive gas to a fuel cell body.

A cell cooling system which controls temperature of a fuel cell body, and an inverter unit connected to an outgoing end of a fuel cell body, Have a dummy resistor connectable between an external load system switch which connects an external load system with this inverter unit, and a fuel electrode of a fuel cell body and an oxidizing agent pole, and at the time of stopping operation. Inert-gas-replacement operation of supplying inactive gas to a fuel cell body from said inert gas feeder, and driving out residual gas at the same time it intercepts supply of reforming fuel from said fuel reformer and said oxidizer feed unit to said fuel cell body, and an oxidizer, Residual voltage control operation which controls residual voltage by supplying said dummy resistor to an outgoing end of said fuel cell body.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to a fuel-cell-power-generation plant which improved to the cell-proper rising-and-falling-temperature control, starting, and stopping timing in deactivation operation of a fuel cell, and a start/stop operation method for the same.
[0002]
[Description of the Prior Art]A fuel cell is a power plant which makes the hydrogen produced by reforming natural gas, and oxygen in the air react electrochemically, and carries out direct electricity generation.
It has the feature of generation efficiency and total energy efficiency being high even when it is small-scale, and excelling in environmental harmony nature.
Although this fuel cell is constituted by carrying out the plural laminates of the unit cell which consists of the anode and cathode of an electrode which pinch an electrolyte and this, what development is following most especially now is a phosphoric acid fuel cell which uses phosphoric acid as an electrolyte.
[0003]An example of the fuel-cell-power-generation plant which uses such a phosphoric acid fuel cell is explained below according to drawing 7. First, the anode 2 in which, as for the unit cell of the fuel cell body 1, fuel, such as hydrogen H_2, contacts the back, It is constituted by arranging the cathode 3 with which oxidizers, such as oxygen O_2, contact the back at the both sides on both sides of the matrix (not shown) which is the supporter with which phosphoric acid was impregnated. The anode 2 and the cathode 3 which are electrodes are created by applying the catalyst of platinum etc. to one side of a porous carbon plate.
[0004]In this case, although only the anode 2 and the cathode 3 of the couple are typically shown in the figure, the fuel cell body 1 is constituted by laminating actually two or more unit cells which consist of such the anode 2 and the cathode 3 by turns via the separator which is a gas separating plate. Between the anode 2 and a separator and between the cathode and the separator, the gas stream popular use slot for pouring fuel and an oxidizer which were mentioned above is formed. The temperature of this fuel cell body has composition controlled by the battery-cooling-water system 4 which supplies cooling water by the predetermined value.
[0005]The fuel reformer 5 is connected to the fuel supply route to the anode 2 in this fuel cell body 1. The fuel reformer 5 is a device which it has a reforming catalyst, and the natural gas which contains hydrocarbon in this reforming catalyst is circulated, and is reformed to hydeogen-rich gas by a reforming reaction.
It has the reformer burner 6 for warming, and has the composition that natural gas is supplied via the fuel-supply-cutoff valve 7.
The steam feed route 8 which supplies a steam to the natural gas feed route between the fuel-supply-cutoff valve 7 and the fuel reformer 5 is connected, and the anode N_2 supplying system 9 which supplies nitrogen N_2 is connected. The anode N_2 supply valve 10 is formed in this anode N_2 supplying system 9.

[0006]On the other hand, the blower 12 is connected to the oxidizer supplying system to the cathode 3 via the air supply cutoff valve 11. Here, the cathode N_2 supplying system 13 for supplying nitrogen N_2 is connected to the air supply course between the air supply cutoff valve 11 and the cathode 3. The cathode N_2 supply valve 14 is formed in this cathode N_2 supplying system 13.

[0007]The flueing course 15 of the anode 2 in the fuel cell body 1 and the cathode 3 is connected to the reformer burner 6. In this fuel-cell-power-generation plant, between two electrodes, it is connected in parallel and via the inverter switch 18 and the dummy resistor switch 19, the inverter 16 and the dummy resistor 17 are connected, respectively so that opening and closing are possible.

[0008]The operation of the power generating plant of the above phosphoric acid fuel cells is as follows. First, since the fuel cell body 1 has a portion which performs a chemical reaction and electrochemical reaction by the inside, before starting, it is necessary [it] to carry out temperature up of the temperature of such an active zone, and to make it the allowable temperature range of a reaction. This temperature-up work is done by going up the circulating water temperature of the battery-cooling-water system which performs temperature control of a fuel cell body.

[0009]Next, the mixed gas of natural gas and a steam is supplied to the fuel reformer 5, and H_2 rich gas is generated by the steam reforming reaction. This H_2 rich gas is supplied to the anode 2. On the other hand, the air compressed by the blower 12 is supplied to the cathode 3. And the H_2 rich gas supplied to the anode 2 in this way and the compressed air supplied to the cathode 3 react electrochemically, and air, water, and heat are generated. The gas discharged from the anode 2 and the cathode 3 is supplied to the reformer burner 6 via the flueing course 15, and is emitted after combustion and into the atmosphere.

[0010]Since H_2 rich gas of the anode 2 and the air of the cathode 3 which were supplied during generating operation remain in power generation stop operation, respectively, By supplying nitrogen N_2 which is inactive gas, purge operation which drives out remains H_2 rich gas and remains air is performed. That is, according to power generation stop instructions, the fuel-supply-cutoff valve 7 and the air supply cutoff valve 11 are closed, and the air supply by the side of H_2 rich gas by the side of an anode and a cathode is intercepted. It can come, simultaneously the anode N_2 supply valve 10 and the cathode supply valve 14 are opened, and nitrogen N_2 is supplied to an anode and the cathode 3. Then, H_2 rich gas and air which remained to the anode 2 and the cathode 3 are driven out by nitrogen N_2.

[0011]By the way, in the above phosphoric acid fuel cells, If the cell voltage per unit cell is maintained more than 0.8V by a high temperature state, it will be known that elution or the sintering phenomenon in which it becomes big and rough and activity area decreases will occur in the precious metal catalyst of an electrode surface, and such a sintering phenomenon will reduce a battery characteristic. When the polarity inversion phenomenon in which the cell voltage per unit cell becomes less than 0V arises, disassembly of a battery material arises and big damage is done to a cell. For this reason, management of cell voltage is needed not only under power generation but during starting and stopping operation.

[0012]During starting and stopping operation, especially in stopping operation, the purge of above-mentioned remains H_2 rich gas and air is performed, and cell voltage inhibitory control is performed. That is, the inverter 16 changes the inverter switch 18 and the dummy resistor switch 19, and supplies the dummy resistor 17 in the place which was made to reduce an AC output according to power generation stop instructions, and was reduced even to the minute output whose operation of the inverter 16 becomes impossible.

[0013]The dummy resistor 17 is supplied above arbitrary voltage, for example, a 0.8V/cell, and is controlled to be wide opened below in a 0.5V/cell. Cell voltage is controlled by the nitrogen N_2

purge operation to this dummy resistor 17, the anode 2, and the cathode 3, and management of the cell voltage under stop is completed.

[0014]

[Problem(s) to be Solved by the Invention]However, in the above phosphoric acid fuel cell power generating plants, there is a problem that a catalyst deteriorates at the time of the stopping operation and start manipulation, and a battery characteristic falls. This point is explained below.

[0015]First, in the stopping operation of a phosphoric acid fuel cell power generating plant, When supplying inactive gas and carrying out inert gas replacement of H_2 rich gas of the anode 2 and the air of the cathode 3 which were supplied during generating operation, the time delays of substitution differ between single cells, and at least one single cell changes with positions in the principal surface. Therefore, it receives that single cell voltage falls promptly in such a portion in the small single cell of substitution delay, or a single cell, In such a portion in the large single cell of substitution delay, or a single cell, since it takes time for the Electrochemistry Sub-Division energy of H_2 rich gas and air which is remains reactant gas to be absorbed by the dummy resistor 17, the fall of single cell voltage also takes time. That is, in such a portion in the large single cell of substitution delay, or a single cell, high generating potential, for example, more than 0.8V, will be exposed inside until the Electrochemistry Sub-Division energy of rich gas and air is absorbed by the dummy resistor 17.

[0016]In this case, in the conventional stopping method, since inert gas replacement is carried out at the same time it intercepts the current under operation near the operating temperature of 200 **, the electrode catalyst layer of the large single cell of substitution delay will be exposed to the elevated temperature (near 200 **) and high potential (more than the 0.8V/cell) near operating temperature.

[0017]Since elution or what is called a sintering phenomenon made big and rough occurs in a precious metal catalyst as it mentioned above, when the electrode catalyst layer was exposed to an elevated temperature and high potential in this way, whenever the effective reaction surface product of an electrode catalyst is shutdown, it will decrease gradually, and degradation of an electrode catalyst will be promoted. As a result, the fall of the voltage-current characteristic which is the output characteristics at the time of generating operation is promoted, and the situation of having an adverse effect on the life of a fuel cell occurs. Since the dummy resistor 17 looks at a laminated fuel cell macroscopically and resistance is decided, it does not come to control the rise of the single cell voltage which remains locally in many cases.

[0018]In the start manipulation of a phosphoric acid fuel cell plant on the other hand, When O_2 in the atmosphere carries out diffusion invasion into the anode 2 and the cathode 3 and sticks to the catalyst of the anode 2 and the cathode 3 via the flueing course 15 during the storage after a fuel cell stop, it will be maintained by the high potential beyond the predetermined value of more than 0.8V, for example.

[0019]Since high potential (>0.8V/cell) will be maintained by a high temperature state if temperature up accompanying start manipulation is performed in this state, the sintering phenomenon of a catalyst advances and it leads to the fall of a battery characteristic by catalytic activity area reduction. In this case, since almost comparable O_2 concentration is stagnating during start manipulation at the anode 2 and the cathode 3, the anode 2 and the cathode 3 are held at the same high potential. Since the cell voltage which is both potential difference has satisfied the predetermined pressure value seemingly, dummy resistor 17 feed control which is voltage control operation is not carried out.

[0020]On the other hand, if according to artificers' experiment the electrode potential under deactivation operation separates from the range of 0.3V to 0.8V as shown in drawing 8, cell voltage falls with the deactivation operation, and the result that the performance of a fuel cell falls is obtained. From this, also during deactivation operation, an electrode cell makes 0.3V minimum potential, and makes the meantime the tolerance level of electrode potential by making 0.8V into maximum potential. By however, macro target control which detects the voltage of the present inert-gas-replacement method and the whole fuel cell body, and supplies / opens a

dummy resistor when it sees in micro in connection with the time lag of inerting, as mentioned above. It is very difficult a single cell or to satisfy not only maximum potential but minimum potential locally.
[0021]In the temperature up and temperature fall operation at the time of deactivation, when the temperature change is early, By disclosure of phosphoric acid from the fuel cell lamination member which consists of porous bodies when the phosphoric acid volume in a fuel cell body changes suddenly, or phosphoric acid movement between members. We lose the phosphate retention balance between the fuel cell lamination members decided by the cell-proper design, and are anxious also about the phenomenon which has an adverse effect on a battery life.
[0022]this invention is proposed in order to solve the problem of the above conventional technologies, and it comes out. The purpose is to provide an outstanding fuel-cell-power-generation plant which can be maintained stably, and a start/stop operation method for the same, without preventing degradation of the catalyst at the time or the time of stopping operation, and reducing a battery characteristic.

[0023]
[Means for Solving the Problem]In order to attain the above-mentioned purpose, the invention according to claim 1, A fuel cell body which carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, A cell cooling system which controls temperature of a fuel cell body, and an inverter unit connected to an outgoing end of a fuel cell body, In a start/stop operation method of a fuel-cell-power-generation plant provided with an external load system switch which connects an external load system with this inverter unit, At the time of one at the time of start manipulation of a fuel-cell-power-generation plant, and stopping operation of operations, it is characterized by having a step which carries out idle mode operation. Here, while idle mode operation makes said external load system switch an opened state, it is supplying an output of said fuel cell body only to electric power system of a fuel-cell-power-generation plant within a station, and it is operated by the minimum load equivalent to load of only electric power system within a station.
[0024]A fuel cell body in which the invention according to claim 11 carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, In a fuel-cell-power-generation plant provided with an external load system switch which connects an external load system with a cell cooling system which controls temperature of a fuel cell body, an inverter unit connected to an outgoing end of a fuel cell body, and this inverter unit, It is a fuel-cell-power-generation plant provided with a control means for enforcing a method according to claim 1.
[0025]In an invention of above Claim 1 and 11 descriptions. By carrying out idle mode operation after a generating operation stop or before a generating operation start by external load and the minimum load of only an intercepted fuel cell plant power system within a station. Where all the cells in a fuel cell body are controlled below to upper limit voltage, for example, 0.8V / cell, independent control of the battery-cooling-water system can be carried out, and it can shift to warming operation or temperature fall operation. Interception with external load or shift to external load can be carried out smoothly, without resulting in catalyst de-activation, since an electrode catalyst layer is not exposed to an elevated temperature and high potential immediately after a generating operation stop or before a generating operation start this.
[0026]The invention according to claim 2 is characterized by having the following step in a start/stop operation method of the fuel-cell-power-generation plant according to claim 1 at the time of stopping operation of a fuel-cell-power-generation plant. Namely, a step which controls generating load based on a stop command, and is reduced to said minimum load, In parallel to a step which opens said external load system switch wide, and carries out said idle mode operation after said minimum load attainment, and a step which carries out said idle mode operation, it has a step which controls said cell cooling system and carries out temperature fall operation of said fuel cell body. When said fuel cell body temperature lowers the temperature to idle mode

shutdown temperature set up lower than operating temperature, In parallel to a step which suspends said idle mode operation, and a step which suspends said idle mode operation, it has a step which carries out inert-gas-replacement operation and main part stopping operation including residual voltage control operation. Here, said inert-gas-replacement operation is operation of supplying inactive gas to a fuel cell body, and driving out residual gas at the same time it intercepts supply of reforming fuel from said fuel reformer and said oxidizer feed unit to said fuel cell body, and an oxidizer. Said residual voltage control operation is operation which controls residual voltage by supplying a dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole.

[0027]In the fuel-cell-power-generation plant according to claim 11, an inert gas feeder which supplies inactive gas to said fuel cell body is formed, and the invention according to claim 12. It is a fuel-cell-power-generation plant having provided a dummy resistor connectable between a fuel electrode of said fuel cell body, and an oxidizing agent pole, and said control means's having used these inert gas feeders and dummy resistors, and constituting a method according to claim 2 feasible.

[0028]In an invention of above Claim 2 and 12 descriptions. By carrying out idle mode operation after a generating operation stop by external load and the minimum load of only an intercepted fuel cell plant power system within a station. Where all the cells in a fuel cell body are controlled below to upper limit voltage, for example, 0.8V / cell, independent control of the battery-cooling-water system can be carried out, and temperature fall operation can be carried out. And when cell-proper temperature lowers the temperature to prescribed temperature lower than operating temperature, idle mode operation can be suspended, while intercepting supply of fuel and an oxidizer, inert-gas-replacement operation by inactive gas can be started, and stopping operation which controls residual voltage can be carried out by supplying a dummy resistor. From this, while fuel cell body temperature under idle mode operation is maintained by elevated temperature, all the single cell voltage becomes possible [satisfying an acceptable value]. Since cell-proper temperature is already lower than operating temperature a single cell or even when voltage more than upper limit voltage occurs locally, degradation of a catalyst can be controlled by residual voltage control operation by injection of a dummy resistor at the time of stopping operation after idle mode operation.

[0029]The invention according to claim 3 is characterized by being temperature when said idle mode shutdown temperature reaches a range whose maximum temperature inside said fuel cell body is 150-180 ** in a start/stop operation method of the fuel-cell-power-generation plant according to claim 1.

[0030]At the above inventions according to claim 3, after a generating operation stop, by carrying out idle mode operation, where all the cells in a fuel cell body are controlled below to upper limit voltage, for example, 0.8V / cell, independent control of the battery-cooling-water system can be carried out, and temperature fall operation can be carried out. And when a cell maximum temperature lowers the temperature even at 150-180 **, idle mode operation can be suspended, while intercepting supply fuel and an oxidizer, inert-gas-replacement operation by inactive gas can be started, and stopping operation which controls residual voltage can be carried out by supplying a dummy resistor. From this, while fuel cell body temperature under idle mode operation is maintained by elevated temperature, all the single cell voltage becomes possible [satisfying an acceptable value]. Since a maximum temperature of a cell proper is already reduced to 150-180 ** of temperature ranges which can fully control degradation speed of a catalyst a single cell or even when voltage more than upper limit voltage occurs locally, By residual voltage control operation by injection of a dummy resistor at the time of stopping operation after idle mode operation, catalyst de-activation accompanying stopping operation can fully be controlled.

[0031]In a start/stop operation method of the fuel-cell-power-generation plant according to claim 2, the invention according to claim 4 in a step which carries out temperature fall operation of said fuel cell body, It is characterized by controlling said cell cooling system so that a cell temperature falling speed under said idle mode operation and a cell temperature falling speed of a to [from said main part stopping operation after idle mode operation / a cell storage

temperature] may be maintained in 50 **/h or less.
[0032]In the above inventions according to claim 4, in idle mode operation after a power generation stop, and in temperature fall operation of a series of cells proper to a subsequent cell storage temperature, since the temperature falling speed was restricted [h] in 50 ** /or less, stopping operation can be completed, without causing a rapid phosphoric acid volume change. Since disclosure of phosphoric acid from a fuel cell lamination member which consists of porous bodies, phosphoric acid movement between members, etc. are avoidable, phosphate retention balance between fuel cell lamination members decided by cell-proper design can be prevented from collapsing, and an outstanding battery life can be secured from this.
[0033]The invention according to claim 5 is characterized by having the following step in a start/stop operation method of the fuel-cell-power-generation plant according to claim 1 at the time of start manipulation of a fuel-cell-power-generation plant. Namely, when said fuel cell body temperature carries out temperature up to a step which controls said cell cooling system based on a starting command, and carries out warming operation of said fuel cell body to idle mode start-up temperature set up lower than operating temperature, It has a step which supplies reforming fuel and an oxidizer from said reformer and said oxidizer feed unit to said fuel cell body, respectively, and carries out said idle mode operation. When said fuel cell body temperature reaches operating temperature, said external load system switch is thrown in and it has a step which carries out external start manipulation which outputs electric power to said external load system.
[0034]The invention according to claim 13 is a fuel-cell-power-generation plant, wherein said control means is constituted feasible in a method according to claim 5 in the fuel-cell-power-generation plant according to claim 11.
[0035]In an invention of above Claim 5 and 13 descriptions. By starting idle mode operation at a temperature lower than operating temperature, before exposing an electrode of a high potential state (more than 0.8V) generated during fuel cell storage by oxygen mixed out of the atmosphere in a cell to a high temperature state in which catalyst de-activation advances. All the cells in a fuel cell body can be controlled below to upper limit voltage, for example, 0.8V / cell. From this, degradation of a catalyst can be controlled compared with a case where it is exposed to a high potential state, to operating temperature.
[0036]The invention according to claim 6 is characterized by said idle mode start-up temperature being the temperature of not less than 150 ** in a start/stop operation method of the fuel-cell-power-generation plant according to claim 5.
[0037]An electrode of a high potential state (more than 0.8V) generated during fuel cell storage in the above inventions according to claim 6 by oxygen mixed out of the atmosphere in a cell, Before exposing to a high temperature state in which catalyst de-activation advances, all the cells in a fuel cell body can be controlled below to upper limit voltage, for example, 0.8V / cell, because catalyst de-activation speed starts idle mode operation in a stage which reached temperature of 150 ** which is not yet accelerated. From this, catalyst de-activation accompanying start manipulation can fully be controlled.
[0038]In a start/stop operation method of the fuel-cell-power-generation plant according to claim 5, the invention according to claim 7 in a step which carries out warming operation of said fuel cell body, It is characterized by controlling said cell cooling system so that a cell heating rate from a cell storage temperature to just before said idle mode operation and a cell heating rate under idle mode operation may be maintained in 50 **/h or less.
[0039]In cell-proper warming operation of a series under cell warming operation from a cell storage temperature after starting to just before said idle mode operation, and idle mode operation in the above inventions according to claim 7, Since the warming operation was restricted in 50 **/h or less, warming operation can be completed without causing a rapid phosphoric acid volume change. Since disclosure of phosphoric acid from a fuel cell lamination member which consists of porous bodies, phosphoric acid movement between members, etc. are avoidable, phosphate retention balance between fuel cell lamination members decided by cell-proper design can be prevented from collapsing, and an outstanding battery life can be secured from this.

[0040]In a start/stop operation method of the fuel-cell-power-generation plant according to claim 5, the invention according to claim 8 in a step which carries out warming operation of said fuel cell body, Before fuel cell body temperature reached 100 **, when inactive gas containing 4% or less of hydrogen [a small amount of] is supplied to a fuel electrode of a fuel cell body and cell voltage of said fuel cell body reaches more than voltage control starting potential set up beforehand, It is characterized by controlling residual voltage by supplying a dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole.

[0041]In the fuel-cell-power-generation plant according to claim 13, an inert gas feeder which supplies inactive gas to said fuel cell body is formed, and the invention according to claim 14. It is a fuel-cell-power-generation plant having provided a dummy resistor connectable between a fuel electrode of said fuel cell body, and an oxidizing agent pole, and said control means's having used these inert gas feeders and dummy resistors, and constituting a method according to claim 8 feasible.

[0042]In an invention of above Claim 8 and 14 descriptions. Before an electrode of a high potential state (more than 0.8V) generated by oxygen mixed out of the atmosphere in a cell during fuel cell storage reaches a high temperature state in which catalyst de-activation advances, by supplying a little H_2 to a fuel electrode. Potential of a fuel electrode can be reduced and potential of an oxidizing agent pole can be observed as a pressure value. And when it reaches more than voltage control starting potential to which a pressure value observed was set beforehand, potential of an oxidizing agent pole can be controlled by supplying a dummy resistor and consuming O_2 in an oxidizing agent pole. From this, an elevated temperature accompanying temperature up and catalyst de-activation which advances in the state of high potential can be prevented.

[0043]A fuel cell body in which the invention according to claim 9 carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, A cell cooling system which controls temperature of a fuel cell body, and an inverter unit connected to an outgoing end of a fuel cell body, It is related with a stopping operation method of a fuel-cell-power-generation plant for carrying out stopping operation of a fuel-cell-power-generation plant provided with an external load system switch which connects an external load system with this inverter unit. And inert-gas-replacement operation of supplying inactive gas to a fuel cell body, and driving out residual gas at the same time it intercepts supply of reforming fuel from said fuel reformer and said oxidizer feed unit to said fuel cell body, and an oxidizer especially, In a stopping operation method of a fuel-cell-power-generation plant provided with a step which carries out main part stopping operation including residual voltage control operation which controls residual voltage by supplying a dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole, It is characterized by said inactive gas of said fuel cell body supplied to either a fuel electrode or an oxidizing agent pole at least containing 0.1% or less of oxygen [a small amount of].

[0044]A fuel cell body in which the invention according to claim 15 carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, An inert gas feeder which supplies inactive gas to a fuel cell body, and a cell cooling system which controls temperature of a fuel cell body, An external load system switch which connects an external load system with an inverter unit connected to an outgoing end of a fuel cell body, and this inverter unit, In a fuel-cell-power-generation plant provided with a dummy resistor connectable between a fuel electrode of a fuel cell body, and an oxidizing agent pole, It is characterized by said inactive gas of said fuel cell body supplied to either a fuel electrode or an oxidizing agent pole at least containing 0.1% or less of oxygen [a small amount of] from said inert gas feeder.

[0045]In an invention of above Claim 9 and 15 descriptions, since 0.1% or less of oxygen [a small amount of] is contained in inactive gas where inert gas replacement by inactive gas is carried out, electrode potential will be in a potential state which is balancing the minute amount oxygen,

i.e., the range of 0.3-0.8V. From this, since electrode potential after stopping operation is manageable within suitable limits, catalyst de-activation can be controlled.

[0046]The invention according to claim 10 is characterized by an oxygen density in said inactive gas being 0.005 to 0.05% in a stopping operation method of the fuel-cell-power-generation plant according to claim 9.

[0047]In the above inventions according to claim 10, where inert-gas-replacement operation by inactive gas is carried out, since an oxygen density in inactive gas is contained 0.001 to 0.1%, balanced maintenance of the electrode potential can be certainly carried out within the limits of 0.3-0.8V. From this, since electrode potential after stopping operation is maintainable within suitable limits, catalyst de-activation can be controlled.

[0048]

[Embodiment of the Invention]Below, the embodiment of a fuel-cell-power-generation plant by this invention, and starting and the stopping method for the same is concretely described with reference to Drawings. The same numerals are given to the same member as the conventional technology shown in drawing 7, and the explanation is omitted.

[0049](1) Describe below one embodiment which applied the 1st embodiment Claim 3 and the invention of 12 descriptions with reference to drawing 1 as a 1st embodiment.

[0050](Elements of the Invention) The composition of the fuel-cell-power-generation plant concerning this embodiment is explained first. That is, as shown in drawing 1, in addition to the inverter (inverter unit) 16 and the dummy resistor 17 which were connected via the inverter switch 18 and the dummy resistor switch 19, respectively, between the anode 2 and the cathode 3, the voltage detection circuits 20 are connected in parallel. And in the ac output line of the inverter 16. The electric power system 21 within a station which supplies a part of fuel cell output, and the external load system of 22 lines which supplies a fuel cell output outside are connected to electric power within a station in parallel, and via the within-a-station electric-power-system switch 23 and the external load system switch 24, it is connected, respectively so that opening and closing are possible.

[0051]The temperature sensor 25 which measures temperature to the inlet section of the cathode 3 of the single cell in the hot spot in the lamination single cell, for example, the lamination station most distant from the cold plate in a layer built cell, is arranged at the fuel cell body 1. In this case, the anode N_2 supplying system 9 and the cathode N_2 supplying system 13 are connected to anode 2 entrance and cathode 3 entrance like the conventional technology shown in drawing 7 via the anode N_2 supply valve 10 and the cathode N_2 supply valve 14.

[0052]In addition to the above composition, the control device (control means) 26 which has a control facility of various sorts is formed. Namely, the battery temperature control facility in which the control device 26 controls battery temperature by giving an output to the battery-cooling-water system 4 with the detection value of the temperature sensor 25, The reactant gas supply control function which controls opening and closing of the inverter opening-and-closing-control function which controls opening and closing of the inverter switch 18, the fuel-supply-cutoff valve 7, and the air supply cutoff valve 11, The inactive gas supply control function which controls opening and closing of the anode N_2 supply valve 10 and the cathode N_2 supply valve 14, From the detection value of the voltage detection circuits 20, it has a system opening-and-closing-control function etc. which control the external load system switch 24 and the within-a-station electric-power-system switch 23 which perform injection/interception to the dummy resistor opening-and-closing-control function, the external load system 22, and the electric power system 21 within a station which control opening and closing of the dummy resistor switch 19.

[0053](OPERATION) The operation of this embodiment which has the above composition is as follows. That is, when a stop command is inputted, the control device 26 orders it load reduction operation to the minimum load of electric power within a station with the shift to a halt condition from a generating operation state. After the minimum load level attainment, while the control device 26 gives an opening signal to the external load system switch 24 and separates an external load system, it holds a closed signal to the within-a-station electric-power-system

switch 23, and carries out idle mode operation by the minimum load level of only the electric power system 21 within a station.

[0054]In this case, since all the lamination single cells of the fuel cell body 1 are load levels with which it is satisfied of below a 0.8V/cell, the catalyst de-activation accompanying sintering does not advance. Since it can be satisfied also with sufficiently small load (current density 10 mA/sq.cm grade) of the cell voltage below 0.8V / cell if it is generally a plant of ordinary pressure operation, the voltage control below 0.8V / cell by a within-a-station electric-power-system load value can be attained easily.

[0055]The control device 26 gives a temperature fall signal to the battery-cooling-water system 4 based on a stop command, and carries out temperature fall operation of the fuel cell body 1 in parallel to idle mode operation. In this case, the temperature sensor 25 detects continuously the hot spot temperature of the fuel cell body 1 under idle mode operation, and continues transmitting a detection value to the control device 26.

[0056]And the detection values from the temperature sensor 25 are the range of 150-180 ** which is the idle mode shutdown temperature set up lower than operating temperature, and the stage which reached 150 ** desirably, The control device 26 gives a full-close signal to the fuel-supply-cutoff valve 7 and the air supply cutoff valve 11, and intercepts fuel and air supply at the same time it gives an opening signal to the within-a-station electric-power-system switch 23 and the inverter switch 18 and carries out fuel cell load shutdown. In parallel to this reactant gas supply interception control, further, the control device 26 gives an opening signal to the N_2 supply valves 10 and 14 of an anode inlet and a cathode inlet with an inactive gas supply control function, and carries out inert-gas-replacement operation by N_2 to the anode 2 and the cathode 3.

[0057]Although residual voltage occurs with remains H_2 rich gas of the anode 2, and the remains air of the cathode 3 at this time, this residual voltage is detected by the voltage detection circuits 20, and is transmitted to the control device 26, and inhibitory control of cell voltage is carried out. That is, when the detection value from the voltage detection circuits 20 exceeds a predetermined value, for example a 0.8V/cell is exceeded, the control device 26 gives an injection signal to the dummy resistor switch 19, forms the circuit by the dummy resistor 17, is consuming a cell output and controls cell voltage.

[0058]By the above operation, power generation stop operation of fuel cell body 1 self is completed (although the power generation operation to the external load system 22 has already stopped, power generation operation of fuel cell body 1 self is completed to this timing). The control device 26 continues the temperature fall operation of the fuel cell body 1 to a cell storage temperature.

[0059](EFFECT OF THE INVENTION) The effect of these above embodiments is as follows. Namely, as for the fuel cell body 1, after interception operation of the external load system 22 accompanying a stop command can manage all lamination single cells to the predetermined value below a 0.8V/cell by carrying out idle mode operation. Therefore, temperature fall operation of the fuel cell body 1 can be carried out good, without the catalyst de-activation by sintering advancing. Although idle mode operation is suspended and de facto battery operation stopping operation is carried out in the stage which the hot spot temperature of the fuel cell body 1 lowered to 150-180 **, In the inert gas replacement by N_2 in this case, and the macroscopic voltage control operation by the dummy resistor 17. Since fuel cell body temperature has already fallen to a predetermined temperature even if the phenomenon of deviating from the predetermined value more than a 0.8V/cell to a part of lamination single cell occurs, the advance grade of the catalyst de-activation by sintering is blunt, and is a permissible grade.

[0060]Drawing 2 is a graph which shows a relation with the catalyst surface product phenomenon ratio showing the battery temperature (catalyst temperature) for which this invention person etc. asked by experiment, and the grade of sintering here, and conditions are electrode potential:0.9V and potential retention time:1h. As shown in this drawing 2, the catalyst surface product reduction ratio accompanying sintering is reducing low temperature greatly, and

when stopping operation time is taken into consideration, the catalyst surface product reduction ratio at 150 **, i.e., the speed of advance of sintering, is in the almost permissible range.
[0061]When the stopping operation in the temperature in which the hot spot of the fuel cell body 1 is lower than 150 ** controls sintering, it is effective enough, but. Reservation of the water-vapor-pressure power currently actually supplied to the fuel reformer 5 from the battery-cooling-water system 4, According to and the reactant gas diffusion defective phenomenon (the phosphoric acid condensed in the low temperature region blockades the reactant gas circulation way of an electrode, and checks the electrochemical reaction of a cell) accompanying condensation of the produced water containing phosphoric acid in the cold spot of the fuel cell body 1. The problem of reducing the problem and battery characteristic on a plant operation will arise.
[0062]Therefore, the hot spot temperature of 150-180 ** of this embodiment and load shutdown operation of the substantial fuel cell body especially in 150 **, Without causing the characteristics degradation accompanied by poor gas diffusion, the stopping operation of the most reliable fuel-cell-power-generation plant that can prevent catalyst de-activation advance can be provided, and practicality is high.
[0063](2) Describe below one embodiment which applied the 2nd embodiment Claim 6 and the invention of 13 descriptions with reference to drawing 3 as a 2nd embodiment.
[0064](Elements of the Invention) The composition of the fuel-cell-power-generation plant concerning this embodiment is explained first. That is, as shown in drawing 3, the point that the voltage detection circuits 20 are connected in parallel in addition to the inverter 16 and the dummy resistor 17 which were connected via the inverter switch 18 and the dummy resistor switch 19 between the anode 2 and the cathode 3, respectively is the same as that of said 1st embodiment. And in the ac output line of the inverter 16. The electric power system 21 within a station which supplies a part of fuel cell output, and the external load system of 22 lines which supplies a fuel cell output outside are connected to electric power within a station in parallel, Respectively, the point connected via the within-a-station electric-power-system switch 23 and the external load system switch 24 so that opening and closing are possible is the same as that of said 1st embodiment.
[0065]On the other hand, the temperature sensor formed in the fuel cell body 1 is limited to the hot spot in a lamination single cell, and is not arranged. In this embodiment, in order to measure the temperature of the fuel cell body 1 in macroscopic, the temperature sensor 27 is arranged at the arbitrary positions in the fuel cell body 1.
[0066]The control device 26 of this embodiment has a control facility of the same various sorts as said 1st embodiment. A control facility actually required of this embodiment, The battery temperature control facility which controls battery temperature by giving an output to the battery-cooling-water system 4 with the detection value of the temperature sensor 27, The reactant gas supply control function which controls opening and closing of the inverter opening-and-closing-control function which controls opening and closing of the inverter switch 18, the fuel-supply-cutoff valve 7, and the air supply cutoff valve 11, It is a system opening-and-closing-control function etc. which control the external load system switch 24 and the within-a-station electric-power-system switch 23 which perform injection/interception to the external load system 22 and the electric power system 21 within a station.
[0067](OPERATION) The operation of this embodiment which has the above composition is as follows. That is, when a starting command is inputted, with the shift to activation status from a fuel cell storage state, the control device 26 gives a temperature-up signal to the battery-cooling-water system 4, and carries out warming operation of the fuel cell body 1. In this case, the temperature sensor 27 detects the temperature of the fuel cell body 1 continuously, and continues transmitting a detection value to the control device 26.
[0068]And when the detection value from the temperature sensor 27, i.e., the temperature of the fuel cell body 1, reaches 150 **, the control device 26 carries out the shift to idle mode operation. That is, H_2 rich gas is introduced from the fuel reformer 5 to the anode 2 by the open operation of the fuel-supply-cutoff valve 7, and the open operation of the air supply cutoff valve

11 performs the air supply to the cathode 3 after that. the stage which detected the generated voltage of the fuel cell body 1 with the voltage detection circuits 20 and to which the detection value reached the predetermined value, for example, the stage which reached 0.8V / cell. By throwing in the inverter switch 18 and throwing in the within-a-station electric-power-system switch 23, the electric power system of 21 lines within a station is formed, and the load transfer to idle mode operation is completed.
[0069]The control device 26 continues this idle mode operation and the warming operation of the fuel cell body 1 in parallel. And when the temperature of the fuel cell body 1 reaches predetermined operating temperature, for example, 190 **, the control device 26 throws in the external load system switch 24, forms the external load system of 22 lines, and carries out load-up control from idle mode operation. It shifts to generating operation mode in the stage which reached the predetermined external load value, and a series of start manipulation is completed.
[0070](EFFECT OF THE INVENTION) The effect of these above embodiments is as follows. Namely, although the electrode of a high potential state (more than 0.8V) generated in the start of start manipulation by the oxygen mixed out of the atmosphere in the cell during fuel cell storage shifts to a high temperature state in connection with warming operation, On the other hand, all the cells in a fuel cell body can be controlled in below upper limit voltage, and 0.8V / cell by starting idle mode operation, when the catalyst de-activation speed of advance by sintering reaches a still permissible temperature, i.e., 150 **.
[0071]Comparatively in [according to / as said 1st embodiment was described about this / this invention person's etc. experimental result] the high potential state in 150 ** of low temperature, When the speed of advance of sintering is reduced greatly and start manipulation time is taken into consideration compared with about operating temperature, for example, 200 **, it is an almost permissible range.
[0072]As said 1st embodiment was similarly described, when idle mode operation at a temperature lower than 150 ** controls sintering, it is effective enough, but. According to the reactant gas diffusion defective phenomenon accompanying reservation of the water-vapor-pressure power currently actually supplied to the fuel reformer 5 from the battery-cooling-water system 4, and condensation of the produced water containing phosphoric acid in the cold spot of the fuel cell body 1. The problem of reducing the problem and battery characteristic on a plant operation will arise.
[0073]Therefore, load transfer operation of the substantial fuel cell body in the fuel cell temperature of not less than 150 ** as shown in this embodiment, Without causing the characteristics degradation accompanied by poor gas diffusion, the start manipulation of the most reliable fuel-cell-power-generation plant that can prevent catalyst de-activation advance can be provided, and practicality is high.
[0074](3) Describe below one embodiment which applied the invention 3rd given in embodiment Claim 4 as a 3rd embodiment.
[0075](Elements of the Invention) In said 1st embodiment shown in drawing 1, the fuel-cell-power-generation plant concerning this embodiment is first characterized by the control device 26 having the function to control the battery-cooling-water system 4 so that the temperature falling speed of battery-cooling-water temperature becomes [h] in 50 ** /or less further. It is constituted by other portions completely like said 1st embodiment.
[0076](OPERATION) An operation of this embodiment which has the above composition is explained below. That is, when a stop command is inputted, the control device 26 orders it load reduction operation to the minimum load of electric power within a station with the shift to a halt condition from a generating operation state. After the minimum load level attainment, while the control device 26 gives an opening signal to the external load system switch 24 and separates an external load system, it holds a closed signal to the within-a-station electric-power-system switch 23, and carries out idle mode operation by the minimum load level of only the electric power system 21 within a station.
[0077]The control device 26 gives a temperature fall signal to the battery-cooling-water system 4 based on a stop command, and in parallel to idle mode operation, as the temperature falling speed of cooling water maintainsh in 50 ** /or less, it carries out temperature fall operation of

the fuel cell body 1. In this case, the temperature sensor 25 detects the temperature of the fuel cell body 1 continuously, and continues transmitting a detection value to the control device 26.
[0078]And the detection values from the temperature sensor 25 are the range of 150-180 **, and the stage which reached 150 ** desirably, and the control device 26, A full-close signal is given to the fuel-supply-cutoff valve 7 and the air supply cutoff valve 11, and fuel and air supply are intercepted at the same time it gives an opening signal to the within-a-station electric-power-system switch 23 and the inverter switch 18 and carries out fuel cell load shutdown. In parallel to this reactant gas supply interception control, further, the control device 26 gives an opening signal to the N_2 supply valves 10 and 14 of an anode inlet and a cathode inlet with an inactive gas supply control function, and carries out inert-gas-replacement operation by N_2 to the anode 2 and the cathode 3.
[0079]Although residual voltage occurs with remains H_2 rich gas of the anode 2, and the remains air of the cathode 3 at this time, this residual voltage is detected by the voltage detection circuits 20, and is transmitted to the control device 26, and inhibitory control of cell voltage is carried out. That is, when the detection value from the voltage detection circuits 20 exceeds a predetermined value, for example the control device 26 exceeds a 0.8V/cell, an injection signal is given to the dummy resistor switch 19, the circuit by the dummy resistor 17 is formed, it is consuming a cell output and control of cell voltage is carried out. By the above operation, although power generation stop operation of fuel cell body 1 self is completed, The control device 26 continues the temperature fall operation of the battery-cooling-water system 4, controlling so that not only the temperature falling speed under idle mode operation but the temperature falling speed from the power generation stop operation after an idle mode to a cell storage temperature maintainsh in 50 ** /or less.
[0080]according to these above embodiments -- the effect of said 1st embodiment -- in addition, the still more nearly following effects are acquired. That is, in idle mode operation after a power generation stop, and in the temperature fall operation of a series of cells proper to a subsequent cell storage temperature, stopping operation can be completed by restricting [h] the temperature falling speed in 50 ** /or less, without causing a rapid phosphoric acid volume change.
[0081]Therefore, since disclosure of phosphoric acid from the fuel cell lamination member which consists of porous bodies, phosphoric acid movement between members, etc. are avoidable, the phosphate retention balance between the fuel cell lamination members decided by the cell-proper design can be prevented from collapsing, and the outstanding battery life can be secured.
[0082](4) Describe below one embodiment which applied the invention 4th given in embodiment Claim 7 as a 4th embodiment.
[0083](Elements of the Invention) In said 2nd embodiment shown in drawing 3, the fuel-cell-power-generation plant concerning this embodiment is first characterized by the control device 26 having the function to control the battery-cooling-water system 4 so that the heating rate of battery-cooling-water temperature becomes [h] in 50 ** /or less further. It is constituted by other portions completely like said 2nd embodiment.
[0084](OPERATION) An operation of this embodiment which has the above composition is explained below. That is, when a starting command is inputted, with the shift to activation status from a fuel cell storage state, the control device 26 gives a temperature-up signal to the battery-cooling-water system 4, and carries out warming operation of the fuel cell body 1. In this case, as the heating rate of cooling water maintains the control device 26 in 50 **/h or less, it carries out warming operation of the fuel cell body 1. In this case, the temperature sensor 27 detects the temperature of the fuel cell body 1 continuously, and continues transmitting a detection value to the control device 26.
[0085]And when the detection value from the temperature sensor 27, i.e., the temperature of the fuel cell body 1, reaches 150 **, the control device 26 carries out the shift to idle mode operation. The control device 26 continues this idle mode operation and the warming operation of the cell proper 1 in parallel, Like the cell heating rate from a cell storage temperature to just before idle mode operation, warming operation of the battery-cooling-water system 4 is carried

out so that the cell heating rate under idle mode operation may satisfyh in 50 ** /or less.
[0086]Next, when the temperature of the fuel cell body 1 reaches predetermined operating temperature, for example, 190 **, the control device 26 throws in the external load system switch 24, forms the external load system of 22 lines, and carries out load-up control from idle mode operation. It shifts to generating operation mode in the stage which reached the predetermined external load value, and a series of start manipulation is completed.
[0087]according to these above embodiments -- the effect of said 2nd embodiment -- in addition, the still more nearly following effects are acquired. Namely, in the cell warming operation from the cell storage temperature after starting to just before said idle mode operation, and a series of cell-proper warming operation under idle mode operation, Warming operation can be completed by restricting the warming operation in 50 **/h or less, without causing a rapid phosphoric acid volume change.
[0088]Therefore, since disclosure of phosphoric acid from the fuel cell lamination member which consists of porous bodies, phosphoric acid movement between members, etc. are avoidable, the phosphate retention balance between the fuel cell lamination members decided by the cell-proper design can be prevented from collapsing, and the outstanding battery life can be secured.
[0089](5) Describe below one embodiment which applied the 5th embodiment Claim 8 and the invention of 14 descriptions with reference to drawing 4 as a 5th embodiment.
[0090](Elements of the Invention) In said 2nd embodiment shown in drawing 3, the composition of the fuel-cell-power-generation plant concerning this embodiment adds the composition for supplying a small amount of hydrogen content nitrogen further first. That is, the minute amount H_2 content N_2 supplying system (minute amount hydrogen containing gas feed unit) 29 containing 4% or less of H_2 [a little] is connected to the entrance of the anode 2 via the H_2 content N_2 supply valve 28 in very small quantities. It is constituted by other portions completely like said 2nd embodiment.
[0091](OPERATION) The operation of this embodiment which has the above composition is as follows. That is, when a starting command is inputted, with the shift to activation status from a fuel cell storage state, the control device 26 gives a temperature-up signal to the battery-cooling-water system 4, and carries out warming operation of the fuel cell body 1. In this case, the temperature sensor 27 detects the temperature of the fuel cell body 1 continuously, and continues transmitting a detection value to the control device 26.
[0092]And before the temperature of the fuel cell body 1 reaches 100 **, the control device 26 gives an opening signal to the anode minute amount H_2 content N_2 supply valve 28, and the N_2 gas which contains 4% or less of H_2 [a little] to the anode 2 from the minute amount H_2 content N_2 supplying system 29 is supplied. At this time, since cell storage hollow mind may have invaded, when high-concentration H_2 is supplied, the danger of explosion is in the anode 2, but. Since the H_2 concentration in the N_2 gas supplied to the anode 2 by this embodiment is the concentration below 4% or less of explosion limit, it can be operated safely.
[0093]Supply of the N_2 gas containing 4% or less of such H_2 [a little] reduces the potential of the anode 2, and observation of it is enabled by making potential of the cathode 3 into a pressure value. That is, since supplied H_2 sticks to the catalyst of the anode 2 even when it originates in the oxygen mixed out of the atmosphere in the cell during fuel cell storage and the anode 2 is in a high potential state (more than 0.8V), the anode 2 is reduced up to the 0V neighborhood which is H_2 potential. On the other hand, in a similar manner, since the cathode 3 is in a high potential state, it is that the potential of the anode 2 fell and voltage generates it between the anode 2 and the cathode 3. The voltage detection circuits 20 detect this generated voltage, and continue transmitting a detection value to the control device 26.
[0094]And when a generated voltage reaches more than the predetermined voltage control starting potential value set up beforehand, for example, a 0.7V/cell, the control device 26, An injection signal is given to the dummy resistor switch 19, the dummy resistor 17 is supplied, by

consuming mixing O_2 in the cathode 3, voltage is reduced and cathode 3 electrode potential is controlled.
[0095]according to these above embodiments -- the effect of said 2nd embodiment -- in addition, the still more nearly following effects are acquired. Namely, the electrode of a high potential state (more than 0.8V) generated in warming operation by the oxygen mixed out of the atmosphere in the cell cell during fuel cell storage, Before reaching the not less than 100 ** high temperature state in which catalyst de-activation advances, cathode potential can be controlled by reducing anode potential, and supplying the dummy resistor 17, and consuming O_2 in the cathode 3 by supplying 4% or less of H_2 [a little] to the anode 2. Therefore, the elevated temperature accompanying temperature up and the catalyst de-activation which advances in the state of high potential can be prevented thoroughly.
[0096](6) Describe below one embodiment which applied the 6th embodiment Claim 10 and the invention of 15 descriptions with reference to drawing 5 as a 6th embodiment.
[0097](Elements of the Invention) In said 1st embodiment shown in drawing 1, the composition of the fuel-cell-power-generation plant used for this embodiment adds the composition for mixing a small amount of air in the cathode 3 side further first. That is, the cathode air supply system 31 is connected upstream of the cathode N_2 supply valve 14 arranged at the entrance of the cathode 3 via the cathode aeration regulating valve 30. Here, when the cathode N_2 supply valve 14 carries out an open operation and N_2 is supplied to the cathode 3, the cathode aeration regulating valve 30 is constituted so that the cathode aeration regulating valve 30 may carry out an open operation simultaneously with this cathode N_2 supply valve 14. The valve opening of the cathode aeration regulating valve 30 in this open operation is adjusted so that the O_2 concentration in the N_2 gas supplied to the cathode 3 may satisfy 0.005 to 0.05%, and that control is carried out by the control device 26. It is constituted by other portions completely like said 1st embodiment.
[0098](OPERATION) The operation of this embodiment which has the above composition is as follows. That is, when a stop command is inputted, the control device 26 orders it load reduction operation to the minimum load of electric power within a station with the shift to a halt condition from a generating operation state. After the minimum load level attainment, the control device 26 gives an opening signal to the external load system switch 24, and separates the external load system 22, and holds a closed signal to the within-a-station electric-power-system switch 23, and continues idle mode operation by the minimum load level of only the electric power system 21 within a station.
[0099]The control device 26 gives a temperature fall signal to the battery-cooling-water system 4 simultaneously with a stop command, and carries out temperature fall operation of the fuel cell body 1 in parallel to idle mode operation. In this case, the temperature sensor 25 detects continuously the hot spot of the fuel cell body 1 under idle mode operation, and continues transmitting a detection value to the control device 26.
[0100]And the detection values from the temperature sensor 25 are the range of 150-180 **, and the stage which reached 150 ** desirably, and the control device 26, A full-close signal is given to the fuel-supply-cutoff valve 7 and the air supply cutoff valve 11, and fuel and air supply are intercepted at the same time it gives an opening signal to the within-a-station electric-power-system switch 23 and the inverter switch 18 and carries out fuel cell load shutdown. In parallel to this reactant gas supply interception control, further, the control device 26 gives an opening signal to the N_2 supply valves 10 and 14 of an anode inlet and a cathode inlet with an inactive gas supply control function, and carries out inert-gas-replacement operation by N_2 to the anode 2 and the cathode 3.
[0101]Although residual voltage occurs with remains H_2 rich gas of the anode 2, and the remains air of the cathode 3 at this time, this residual voltage is detected by the voltage detection circuits 20, and is transmitted to the control device 26, and inhibitory control of cell voltage is

carried out. That is, when the detection value from the voltage detection circuits 20 exceeds a predetermined value, for example a 0.8V/cell is exceeded, the control device 26 gives an injection signal to the dummy resistor switch 19, forms the circuit by the dummy resistor 17, is consuming a cell output and controls cell voltage.

[0102]When carrying out the open operation of the cathode N_2 supply valve 14 as mentioned above and supplying N_2 to the cathode 3 in this embodiment, the control device 26, In order that the open operation also of the cathode aeration regulating valve 30 may be carried out and it may control the valve opening simultaneously with the cathode N_2 supply valve 14, N_2 which contains 0.005 to 0.05% of O_2 in the cathode 3 from the cathode air supply system 31 is supplied. Thus, the electrode potential of the cathode 3 maintains the range of 0.3-0.8V certainly by supplying O_2 of 0.005 to 0.05% of concentration.

[0103]By the above operation, although power generation stop operation of fuel cell body 1 self is completed, the control device 26 continues the temperature fall operation of the fuel cell body 1 to a cell storage temperature.

[0104]according to these above embodiments -- the effect of said 1st embodiment -- in addition, the still more nearly following effects are acquired. That is, since a small amount of oxygen is contained in inactive gas where inert-gas-replacement operation by the inactive gas accompanying stopping operation is carried out, electrode potential is maintained by the potential state which is balancing the minute amount oxygen.

[0105]Drawing 6 shows the relation of the O_2 concentration and electrode potential for which this invention person etc. asked by experiment. As shown in drawing 6, the relation between O_2 concentration and electrode potential changes with catalyst presentations (this is determined with the mixed potential of the precious metals and carbon which are catalyst presentations). On the other hand, as mentioned above, drawing 8 shows the electrode potential after stopping operation, and the relation of the amount of sag accompanying the stopping operation.

[0106]Also in about various catalyst presentations, the electrode potential in 0.001 to 0.1% of an oxygen density shows 0.3-0.8V, and it is clearer than the graph of these drawing 6 and drawing 8 that this potential range's sag accompanying stopping operation can be controlled. That is, when electrode potential exceeds 0.8V. In order that sintering of a catalyst may accelerate, cause the sag accompanying stopping operation, and when electrode potential is less than 0.3V, on the other hand, The catalyst precious metals which dissolved by sintering re-deposit, catalytic activity area decreases the active site of a catalyst to a wrap sake, and it is thought that the sag accompanying stopping operation is caused.

[0107]Therefore, after a power generation stop, when the oxygen density in inactive gas is 0.001 to 0.1%, electrode potential can be held to 0.3-0.8V, and a catalyst de-activation phenomenon which was mentioned above can be avoided. In particular, like this embodiment, when an oxygen density is limited to 0.005 to 0.05%, it is not concerned with a catalyst presentation but electrode potential can be certainly held to 0.3-0.8V so that clearly from drawing 6.

[0108]Although this embodiment makes a little O_2 mix into N_2 for a purge of the cathode 3, it can acquire the same effect about an anode catalyst similarly by making a little O_2 mix in N_2 for a purge of the anode 2. When a little O_2 are made to mix in one of N_2 for a purge of the anode 2 and the cathode 3, Although in O_2 some time lag (about 10 min) produces the electrolyte layer between the anode 2 and the cathode 3 in order to carry out spreading diffusion, the dissolution and, two poles can hold the electrode potential which balances a little O_2.

[0109](7) Other embodiment this inventions are not limited to the above embodiments. For example, as mentioned above, each embodiment has a clear effect, but it is possible by combining two or more aforementioned embodiments suitably to acquire a synergistic effect. It is selectable suitably in the concrete composition of each part, such as a control device, a supply valve, a supplying system.

[0110]

[Effect of the Invention]Since the voltage of a fuel cell body can fully be controlled by carrying out idle mode operation of only electric power system within a station, or making a small amount of hydrogen and minute amount oxygen contain in the inactive gas for inert gas replacement according to this invention as explained above, Degradation of the catalyst at the time of start manipulation and stopping operation is prevented, and an outstanding fuel-cell-power-generation plant, and starting and the stopping method for the same which can be maintained stably can be provided, without reducing the battery characteristic accompanying deactivation operation.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention]This invention relates to a fuel-cell-power-generation plant which improved to the cell-proper rising-and-falling-temperature control, starting, and stopping timing in deactivation operation of a fuel cell, and a start/stop operation method for the same.

[Translation done.]

PRIOR ART

[Description of the Prior Art]A fuel cell is a power plant which makes the hydrogen produced by reforming natural gas, and oxygen in the air react electrochemically, and carries out direct electricity generation.
It has the feature of generation efficiency and total energy efficiency being high even when it is small-scale, and excelling in environmental harmony nature.
Although this fuel cell is constituted by carrying out the plural laminates of the unit cell which consists of the anode and cathode of an electrode which pinch an electrolyte and this, what development is following most especially now is a phosphoric acid fuel cell which uses phosphoric acid as an electrolyte.
[0003]An example of the fuel-cell-power-generation plant which uses such a phosphoric acid fuel cell is explained below according to drawing 7. First, the anode 2 in which, as for the unit cell of the fuel cell body 1, fuel, such as hydrogen H_2, contacts the back, It is constituted by arranging the cathode 3 with which oxidizers, such as oxygen O_2, contact the back at the both sides on both sides of the matrix (not shown) which is the supporter with which phosphoric acid was impregnated. The anode 2 and the cathode 3 which are electrodes are created by applying the catalyst of platinum etc. to one side of a porous carbon plate.
[0004]In this case, although only the anode 2 and the cathode 3 of the couple are typically shown in the figure, the fuel cell body 1 is constituted by laminating actually two or more unit cells which consist of such the anode 2 and the cathode 3 by turns via the separator which is a gas separating plate. Between the anode 2 and a separator and between the cathode and the separator, the gas stream popular use slot for pouring fuel and an oxidizer which were mentioned above is formed. The temperature of this fuel cell body has composition controlled by the battery-cooling-water system 4 which supplies cooling water by the predetermined value.
[0005]The fuel reformer 5 is connected to the fuel supply route to the anode 2 in this fuel cell body 1. The fuel reformer 5 is a device which it has a reforming catalyst, and the natural gas which contains hydrocarbon in this reforming catalyst is circulated, and is reformed to hydeogen-rich gas by a reforming reaction.
It has the reformer burner 6 for warming, and has the composition that natural gas is supplied via the fuel-supply-cutoff valve 7.
The steam feed route 8 which supplies a steam to the natural gas feed route between the fuel-supply-cutoff valve 7 and the fuel reformer 5 is connected, and the anode N_2 supplying system 9 which supplies nitrogen N_2 is connected. The anode N_2 supply valve 10 is formed in this anode N_2 supplying system 9.
[0006]On the other hand, the blower 12 is connected to the oxidizer supplying system to the cathode 3 via the air supply cutoff valve 11. Here, the cathode N_2 supplying system 13 for supplying nitrogen N_2 is connected to the air supply course between the air supply cutoff valve 11 and the cathode 3. The cathode N_2 supply valve 14 is formed in this cathode N_2 supplying system 13.

[0007]The flueing course 15 of the anode 2 in the fuel cell body 1 and the cathode 3 is connected to the reformer burner 6. In this fuel-cell-power-generation plant, between two electrodes, it is connected in parallel and via the inverter switch 18 and the dummy resistor switch 19, the inverter 16 and the dummy resistor 17 are connected, respectively so that opening and closing are possible.
[0008]The operation of the power generating plant of the above phosphoric acid fuel cells is as follows. First, since the fuel cell body 1 has a portion which performs a chemical reaction and electrochemical reaction by the inside, before starting, it is necessary [it] to carry out temperature up of the temperature of such an active zone, and to make it the allowable temperature range of a reaction. This temperature-up work is done by going up the circulating water temperature of the battery-cooling-water system which performs temperature control of a fuel cell body.
[0009]Next, the mixed gas of natural gas and a steam is supplied to the fuel reformer 5, and H_2 rich gas is generated by the steam reforming reaction. This H_2 rich gas is supplied to the anode 2. On the other hand, the air compressed by the blower 12 is supplied to the cathode 3. And the H_2 rich gas supplied to the anode 2 in this way and the compressed air supplied to the cathode 3 react electrochemically, and air, water, and heat are generated. The gas discharged from the anode 2 and the cathode 3 is supplied to the reformer burner 6 via the flueing course 15, and is emitted after combustion and into the atmosphere.
[0010]Since H_2 rich gas of the anode 2 and the air of the cathode 3 which were supplied during generating operation remain in power generation stop operation, respectively, By supplying nitrogen N_2 which is inactive gas, purge operation which drives out remains H_2 rich gas and remains air is performed. That is, according to power generation stop instructions, the fuel-supply-cutoff valve 7 and the air supply cutoff valve 11 are closed, and the air supply by the side of H_2 rich gas by the side of an anode and a cathode is intercepted. It can come, simultaneously the anode N_2 supply valve 10 and the cathode supply valve 14 are opened, and nitrogen N_2 is supplied to an anode and the cathode 3. Then, H_2 rich gas and air which remained to the anode 2 and the cathode 3 are driven out by nitrogen N_2.
[0011]By the way, in the above phosphoric acid fuel cells, If the cell voltage per unit cell is maintained more than 0.8V by a high temperature state, it will be known that elution or the sintering phenomenon in which it becomes big and rough and activity area decreases will occur in the precious metal catalyst of an electrode surface, and such a sintering phenomenon will reduce a battery characteristic. When the polarity inversion phenomenon in which the cell voltage per unit cell becomes less than 0V arises, disassembly of a battery material arises and big damage is done to a cell. For this reason, management of cell voltage is needed not only under power generation but during starting and stopping operation.
[0012]During starting and stopping operation, especially in stopping operation, the purge of above-mentioned remains H_2 rich gas and air is performed, and cell voltage inhibitory control is performed. That is, the inverter 16 changes the inverter switch 18 and the dummy resistor switch 19, and supplies the dummy resistor 17 in the place which was made to reduce an AC output according to power generation stop instructions, and was reduced even to the minute output whose operation of the inverter 16 becomes impossible.
[0013]The dummy resistor 17 is supplied above arbitrary voltage, for example, a 0.8V/cell, and is controlled to be wide opened below in a 0.5V/cell. Cell voltage is controlled by the nitrogen N_2 purge operation to this dummy resistor 17, the anode 2, and the cathode 3, and management of the cell voltage under stop is completed.

[Translation done.]

EFFECT OF THE INVENTION

(EFFECT OF THE INVENTION) The effect of these above embodiments is as follows. Namely, as for the fuel cell body 1, after interception operation of the external load system 22 accompanying a stop command can manage all lamination single cells to the predetermined value below a 0.8V/cell by carrying out idle mode operation. Therefore, temperature fall operation of the fuel cell body 1 can be carried out good, without the catalyst de-activation by sintering advancing. Although idle mode operation is suspended and de facto battery operation stopping operation is carried out in the stage which the hot spot temperature of the fuel cell body 1 lowered to 150-180 **, In the inert gas replacement by N_2 in this case, and the macroscopic voltage control operation by the dummy resistor 17. Since fuel cell body temperature has already fallen to a predetermined temperature even if the phenomenon of deviating from the predetermined value more than a 0.8V/cell to a part of lamination single cell occurs, the advance grade of the catalyst de-activation by sintering is blunt, and is a permissible grade.
[0060]Here, drawing 2 is a graph which shows a relation with the catalyst surface product phenomenon ratio showing the battery temperature (catalyst temperature) for which this invention person etc. asked by experiment, and the grade of sintering.
Conditions are electrode potential:0.9V and potential retention time:1h.
As shown in this drawing 2, the catalyst surface product reduction ratio accompanying sintering is reducing low temperature greatly, and when stopping operation time is taken into consideration, the catalyst surface product reduction ratio at 150 **, i.e., the speed of advance of sintering, is in the almost permissible range.
[0061]When the stopping operation in the temperature in which the hot spot of the fuel cell body 1 is lower than 150 ** controls sintering, it is effective enough, but. Reservation of the water-vapor-pressure power currently actually supplied to the fuel reformer 5 from the battery-cooling-water system 4, According to and the reactant gas diffusion defective phenomenon (the phosphoric acid condensed in the low temperature region blockades the reactant gas circulation way of an electrode, and checks the electrochemical reaction of a cell) accompanying condensation of the produced water containing phosphoric acid in the cold spot of the fuel cell body 1. The problem of reducing the problem and battery characteristic on a plant operation will arise.
[0062]Therefore, the hot spot temperature of 150-180 ** of this embodiment and load shutdown operation of the substantial fuel cell body especially in 150 **, The stopping operation of the most reliable fuel-cell-power-generation plant that can prevent catalyst de-activation advance can be provided without causing the characteristics degradation accompanied by poor gas diffusion.
Practicality is high.

[0063](2) Describe below one embodiment which applied the 2nd embodiment Claim 6 and the invention of 13 descriptions with reference to drawing 3 as a 2nd embodiment.
[0064](Elements of the Invention) Composition of a fuel-cell-power-generation plant concerning this embodiment is explained first. That is, as shown in drawing 3, a point that the voltage detection circuits 20 are connected in parallel in addition to the inverter 16 and the dummy

resistor 17 which were connected via the inverter switch 18 and the dummy resistor switch 19 between the anode 2 and the cathode 3, respectively is the same as that of said 1st embodiment. And in an ac output line of the inverter 16. The electric power system 21 within a station which supplies a part of fuel cell output, and an external load system of 22 lines which supplies a fuel cell output outside are connected to electric power within a station in parallel, Respectively, a point connected via the within-a-station electric-power-system switch 23 and the external load system switch 24 so that opening and closing are possible is the same as that of said 1st embodiment.

[0065]On the other hand, a temperature sensor formed in the fuel cell body 1 is limited to a hot spot in a lamination single cell, and is not arranged. In this embodiment, in order to measure temperature of the fuel cell body 1 in macroscopic, the temperature sensor 27 is arranged at arbitrary positions in the fuel cell body 1.

[0066]The control device 26 of this embodiment has a control facility of the same various sorts as said 1st embodiment. A control facility actually required of this embodiment, The battery temperature control facility which controls battery temperature by giving an output to the battery-cooling-water system 4 with the detection value of the temperature sensor 27, The reactant gas supply control function which controls opening and closing of the inverter opening-and-closing-control function which controls opening and closing of the inverter switch 18, the fuel-supply-cutoff valve 7, and the air supply cutoff valve 11, It is a system opening-and-closing-control function etc. which control the external load system switch 24 and the within-a-station electric-power-system switch 23 which perform injection/interception to the external load system 22 and the electric power system 21 within a station.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, in the above phosphoric acid fuel cell power generating plants, there is a problem that a catalyst deteriorates at the time of the stopping operation and start manipulation, and a battery characteristic falls. This point is explained below.
[0015]First, in the stopping operation of a phosphoric acid fuel cell power generating plant, When supplying inactive gas and carrying out inert gas replacement of H_2 rich gas of the anode 2 and the air of the cathode 3 which were supplied during generating operation, the time delays of substitution differ between single cells, and at least one single cell changes with positions in the principal surface. Therefore, it receives that single cell voltage falls promptly in such a portion in the small single cell of substitution delay, or a single cell, In such a portion in the large single cell of substitution delay, or a single cell, since it takes time for the Electrochemistry Sub-Division energy of H_2 rich gas and air which is remains reactant gas to be absorbed by the dummy resistor 17, the fall of single cell voltage also takes time. That is, in such a portion in the large single cell of substitution delay, or a single cell, high generating potential, for example, more than 0.8V, will be exposed inside until the Electrochemistry Sub-Division energy of rich gas and air is absorbed by the dummy resistor 17.
[0016]In this case, in the conventional stopping method, since inert gas replacement is carried out at the same time it intercepts the current under operation near the operating temperature of 200 **, the electrode catalyst layer of the large single cell of substitution delay will be exposed to the elevated temperature (near 200 **) and high potential (more than the 0.8V/cell) near operating temperature.
[0017]Since elution or what is called a sintering phenomenon made big and rough occurs in a precious metal catalyst as it mentioned above, when the electrode catalyst layer was exposed to an elevated temperature and high potential in this way, whenever the effective reaction surface product of an electrode catalyst is shutdown, it will decrease gradually, and degradation of an electrode catalyst will be promoted. As a result, the fall of the voltage-current characteristic which is the output characteristics at the time of generating operation is promoted, and the situation of having an adverse effect on the life of a fuel cell occurs. Since the dummy resistor 17 looks at a laminated fuel cell macroscopically and resistance is decided, it does not come to control the rise of the single cell voltage which remains locally in many cases.
[0018]In the start manipulation of a phosphoric acid fuel cell plant on the other hand, When O_2 in the atmosphere carries out diffusion invasion into the anode 2 and the cathode 3 and sticks to the catalyst of the anode 2 and the cathode 3 via the flueing course 15 during the storage after a fuel cell stop, it will be maintained by the high potential beyond the predetermined value of more than 0.8V, for example.
[0019]Since high potential (>0.8V/cell) will be maintained by a high temperature state if temperature up accompanying start manipulation is performed in this state, the sintering phenomenon of a catalyst advances and it leads to the fall of a battery characteristic by catalytic activity area reduction. In this case, since almost comparable O_2 concentration is stagnating during start manipulation at the anode 2 and the cathode 3, the anode 2 and the cathode 3 are held at the same high potential. Since the cell voltage which is both potential

difference has satisfied the predetermined pressure value seemingly, dummy resistor 17 feed control which is voltage control operation is not carried out.
[0020]On the other hand, if according to artificers' experiment the electrode potential under deactivation operation separates from the range of 0.3V to 0.8V as shown in drawing 8, cell voltage falls with the deactivation operation, and the result that the performance of a fuel cell falls is obtained. From this, also during deactivation operation, an electrode cell makes 0.3V minimum potential, and makes the meantime the tolerance level of electrode potential by making 0.8V into maximum potential. By however, macro target control which detects the voltage of the present inert-gas-replacement method and the whole fuel cell body, and supplies / opens a dummy resistor when it sees in micro in connection with the time lag of inerting, as mentioned above. It is very difficult a single cell or to satisfy not only maximum potential but minimum potential locally.
[0021]In the temperature up and temperature fall operation at the time of deactivation, when the temperature change is early, By disclosure of phosphoric acid from the fuel cell lamination member which consists of porous bodies when the phosphoric acid volume in a fuel cell body changes suddenly, or phosphoric acid movement between members. We lose the phosphate retention balance between the fuel cell lamination members decided by the cell-proper design, and are anxious also about the phenomenon which has an adverse effect on a battery life.
[0022]this invention is proposed in order to solve the problem of the above conventional technologies, and it comes out. The purpose is to provide an outstanding fuel-cell-power-generation plant which can be maintained stably, and a start/stop operation method for the same, without preventing degradation of the catalyst at the time or the time of stopping operation, and reducing a battery characteristic.

[Translation done.]

MEANS

[Means for Solving the Problem]In order to attain the above-mentioned purpose, the invention according to claim 1, A fuel cell body which carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, A cell cooling system which controls temperature of a fuel cell body, and an inverter unit connected to an outgoing end of a fuel cell body, In a start/stop operation method of a fuel-cell-power-generation plant provided with an external load system switch which connects an external load system with this inverter unit, At the time of one at the time of start manipulation of a fuel-cell-power-generation plant, and stopping operation of operations, it is characterized by having a step which carries out idle mode operation. Here, while idle mode operation makes said external load system switch an opened state, it is supplying an output of said fuel cell body only to electric power system of a fuel-cell-power-generation plant within a station, and it is operated by the minimum load equivalent to load of only electric power system within a station.
[0024]A fuel cell body in which the invention according to claim 11 carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, In a fuel-cell-power-generation plant provided with an external load system switch which connects an external load system with a cell cooling system which controls temperature of a fuel cell body, an inverter unit connected to an outgoing end of a fuel cell body, and this inverter unit, It is a fuel-cell-power-generation plant provided with a control means for enforcing a method according to claim 1.
[0025]In an invention of above Claim 1 and 11 descriptions. By carrying out idle mode operation after a generating operation stop or before a generating operation start by external load and the minimum load of only an intercepted fuel cell plant power system within a station. Where all the cells in a fuel cell body are controlled below to upper limit voltage, for example, 0.8V / cell, independent control of the battery-cooling-water system can be carried out, and it can shift to warming operation or temperature fall operation. Interception with external load or shift to external load can be carried out smoothly, without resulting in catalyst de-activation, since an electrode catalyst layer is not exposed to an elevated temperature and high potential immediately after a generating operation stop or before a generating operation start this.
[0026]The invention according to claim 2 is characterized by having the following step in a start/stop operation method of the fuel-cell-power-generation plant according to claim 1 at the time of stopping operation of a fuel-cell-power-generation plant. Namely, a step which controls generating load based on a stop command, and is reduced to said minimum load, In parallel to a step which opens said external load system switch wide, and carries out said idle mode operation after said minimum load attainment, and a step which carries out said idle mode operation, it has a step which controls said cell cooling system and carries out temperature fall operation of said fuel cell body. When said fuel cell body temperature lowers the temperature to idle mode shutdown temperature set up lower than operating temperature, In parallel to a step which suspends said idle mode operation, and a step which suspends said idle mode operation, it has a step which carries out inert-gas-replacement operation and main part stopping operation

including residual voltage control operation. Here, said inert-gas-replacement operation is operation of supplying inactive gas to a fuel cell body, and driving out residual gas at the same time it intercepts supply of reforming fuel from said fuel reformer and said oxidizer feed unit to said fuel cell body, and an oxidizer. Said residual voltage control operation is operation which controls residual voltage by supplying a dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole.

[0027]In the fuel-cell-power-generation plant according to claim 11, an inert gas feeder which supplies inactive gas to said fuel cell body is formed, and the invention according to claim 12. It is a fuel-cell-power-generation plant having provided a dummy resistor connectable between a fuel electrode of said fuel cell body, and an oxidizing agent pole, and said control means's having used these inert gas feeders and dummy resistors, and constituting a method according to claim 2 feasible.

[0028]In an invention of above Claim 2 and 12 descriptions. By carrying out idle mode operation after a generating operation stop by external load and the minimum load of only an intercepted fuel cell plant power system within a station. Where all the cells in a fuel cell body are controlled below to upper limit voltage, for example, 0.8V / cell, independent control of the battery-cooling-water system can be carried out, and temperature fall operation can be carried out. And when cell-proper temperature lowers the temperature to prescribed temperature lower than operating temperature, idle mode operation can be suspended, while intercepting supply of fuel and an oxidizer, inert-gas-replacement operation by inactive gas can be started, and stopping operation which controls residual voltage can be carried out by supplying a dummy resistor. From this, while fuel cell body temperature under idle mode operation is maintained by elevated temperature, all the single cell voltage becomes possible [satisfying an acceptable value]. Since cell-proper temperature is already lower than operating temperature a single cell or even when voltage more than upper limit voltage occurs locally, degradation of a catalyst can be controlled by residual voltage control operation by injection of a dummy resistor at the time of stopping operation after idle mode operation.

[0029]The invention according to claim 3 is characterized by being temperature when said idle mode shutdown temperature reaches a range whose maximum temperature inside said fuel cell body is 150-180 ** in a start/stop operation method of the fuel-cell-power-generation plant according to claim 1.

[0030]At the above inventions according to claim 3, after a generating operation stop, by carrying out idle mode operation, where all the cells in a fuel cell body are controlled below to upper limit voltage, for example, 0.8V / cell, independent control of the battery-cooling-water system can be carried out, and temperature fall operation can be carried out. And when a cell maximum temperature lowers the temperature even at 150-180 **, idle mode operation can be suspended, while intercepting supply fuel and an oxidizer, inert-gas-replacement operation by inactive gas can be started, and stopping operation which controls residual voltage can be carried out by supplying a dummy resistor. From this, while fuel cell body temperature under idle mode operation is maintained by elevated temperature, all the single cell voltage becomes possible [satisfying an acceptable value]. Since a maximum temperature of a cell proper is already reduced to 150-180 ** of temperature ranges which can fully control degradation speed of a catalyst a single cell or even when voltage more than upper limit voltage occurs locally, By residual voltage control operation by injection of a dummy resistor at the time of stopping operation after idle mode operation, catalyst de-activation accompanying stopping operation can fully be controlled.

[0031]In a start/stop operation method of the fuel-cell-power-generation plant according to claim 2, the invention according to claim 4 in a step which carries out temperature fall operation of said fuel cell body, It is characterized by controlling said cell cooling system so that a cell temperature falling speed under said idle mode operation and a cell temperature falling speed of a to [from said main part stopping operation after idle mode operation / a cell storage temperature] may be maintained in 50 **/h or less.

[0032]In the above inventions according to claim 4, in idle mode operation after a power generation stop, and in temperature fall operation of a series of cells proper to a subsequent cell

storage temperature, since the temperature falling speed was restricted [h] in 50 ** /or less, stopping operation can be completed, without causing a rapid phosphoric acid volume change. Since disclosure of phosphoric acid from a fuel cell lamination member which consists of porous bodies, phosphoric acid movement between members, etc. are avoidable, phosphate retention balance between fuel cell lamination members decided by cell-proper design can be prevented from collapsing, and an outstanding battery life can be secured from this.
[0033]The invention according to claim 5 is characterized by having the following step in a start/stop operation method of the fuel-cell-power-generation plant according to claim 1 at the time of start manipulation of a fuel-cell-power-generation plant. Namely, when said fuel cell body temperature carries out temperature up to a step which controls said cell cooling system based on a starting command, and carries out warming operation of said fuel cell body to idle mode start-up temperature set up lower than operating temperature, It has a step which supplies reforming fuel and an oxidizer from said reformer and said oxidizer feed unit to said fuel cell body, respectively, and carries out said idle mode operation. When said fuel cell body temperature reaches operating temperature, said external load system switch is thrown in and it has a step which carries out external start manipulation which outputs electric power to said external load system.
[0034]The invention according to claim 13 is a fuel-cell-power-generation plant, wherein said control means is constituted feasible in a method according to claim 5 in the fuel-cell-power-generation plant according to claim 11.
[0035]In an invention of above Claim 5 and 13 descriptions. By starting idle mode operation at a temperature lower than operating temperature, before exposing an electrode of a high potential state (more than 0.8V) generated during fuel cell storage by oxygen mixed out of the atmosphere in a cell to a high temperature state in which catalyst de-activation advances. All the cells in a fuel cell body can be controlled below to upper limit voltage, for example, 0.8V / cell. From this, degradation of a catalyst can be controlled compared with a case where it is exposed to a high potential state, to operating temperature.
[0036]The invention according to claim 6 is characterized by said idle mode start-up temperature being the temperature of not less than 150 ** in a start/stop operation method of the fuel-cell-power-generation plant according to claim 5.
[0037]An electrode of a high potential state (more than 0.8V) generated during fuel cell storage in the above inventions according to claim 6 by oxygen mixed out of the atmosphere in a cell, Before exposing to a high temperature state in which catalyst de-activation advances, all the cells in a fuel cell body can be controlled below to upper limit voltage, for example, 0.8V / cell, because catalyst de-activation speed starts idle mode operation in a stage which reached temperature of 150 ** which is not yet accelerated. From this, catalyst de-activation accompanying start manipulation can fully be controlled.
[0038]In a start/stop operation method of the fuel-cell-power-generation plant according to claim 5, the invention according to claim 7 in a step which carries out warming operation of said fuel cell body, It is characterized by controlling said cell cooling system so that a cell heating rate from a cell storage temperature to just before said idle mode operation and a cell heating rate under idle mode operation may be maintained in 50 **/h or less.
[0039]In cell-proper warming operation of a series under cell warming operation from a cell storage temperature after starting to just before said idle mode operation, and idle mode operation in the above inventions according to claim 7, Since the warming operation was restricted in 50 **/h or less, warming operation can be completed without causing a rapid phosphoric acid volume change. Since disclosure of phosphoric acid from a fuel cell lamination member which consists of porous bodies, phosphoric acid movement between members, etc. are avoidable, phosphate retention balance between fuel cell lamination members decided by cell-proper design can be prevented from collapsing, and an outstanding battery life can be secured from this.
[0040]In a start/stop operation method of the fuel-cell-power-generation plant according to claim 5, the invention according to claim 8 in a step which carries out warming operation of said fuel cell body, Before fuel cell body temperature reached 100 **, when inactive gas containing 4%

or less of hydrogen [a small amount of] is supplied to a fuel electrode of a fuel cell body and cell voltage of said fuel cell body reaches more than voltage control starting potential set up beforehand, It is characterized by controlling residual voltage by supplying a dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole.

[0041]In the fuel-cell-power-generation plant according to claim 13, an inert gas feeder which supplies inactive gas to said fuel cell body is formed, and the invention according to claim 14. It is a fuel-cell-power-generation plant having provided a dummy resistor connectable between a fuel electrode of said fuel cell body, and an oxidizing agent pole, and said control means's having used these inert gas feeders and dummy resistors, and constituting a method according to claim 8 feasible.

[0042]In an invention of above Claim 8 and 14 descriptions. Before an electrode of a high potential state (more than 0.8V) generated by oxygen mixed out of the atmosphere in a cell during fuel cell storage reaches a high temperature state in which catalyst de-activation advances, by supplying a little H_2 to a fuel electrode. Potential of a fuel electrode can be reduced and potential of an oxidizing agent pole can be observed as a pressure value. And when it reaches more than voltage control starting potential to which a pressure value observed was set beforehand, potential of an oxidizing agent pole can be controlled by supplying a dummy resistor and consuming O_2 in an oxidizing agent pole. From this, an elevated temperature accompanying temperature up and catalyst de-activation which advances in the state of high potential can be prevented.

[0043]A fuel cell body in which the invention according to claim 9 carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, A cell cooling system which controls temperature of a fuel cell body, and an inverter unit connected to an outgoing end of a fuel cell body, It is related with a stopping operation method of a fuel-cell-power-generation plant for carrying out stopping operation of a fuel-cell-power-generation plant provided with an external load system switch which connects an external load system with this inverter unit. And inert-gas-replacement operation of supplying inactive gas to a fuel cell body, and driving out residual gas at the same time it intercepts supply of reforming fuel from said fuel reformer and said oxidizer feed unit to said fuel cell body, and an oxidizer especially, In a stopping operation method of a fuel-cell-power-generation plant provided with a step which carries out main part stopping operation including residual voltage control operation which controls residual voltage by supplying a dummy resistor between a fuel electrode of said fuel cell body, and an oxidizing agent pole, It is characterized by said inactive gas of said fuel cell body supplied to either a fuel electrode or an oxidizing agent pole at least containing 0.1% or less of oxygen [a small amount of].

[0044]A fuel cell body in which the invention according to claim 15 carries out the plural laminates of the unit cell which consists of a fuel electrode and an oxidizing agent pole, A fuel reformer and an oxidizer feed unit which supply fuel and an oxidizer to this fuel cell body, respectively, An inert gas feeder which supplies inactive gas to a fuel cell body, and a cell cooling system which controls temperature of a fuel cell body, An external load system switch which connects an external load system with an inverter unit connected to an outgoing end of a fuel cell body, and this inverter unit, In a fuel-cell-power-generation plant provided with a dummy resistor connectable between a fuel electrode of a fuel cell body, and an oxidizing agent pole, It is characterized by said inactive gas of said fuel cell body supplied to either a fuel electrode or an oxidizing agent pole at least containing 0.1% or less of oxygen [a small amount of] from said inert gas feeder.

[0045]In an invention of above Claim 9 and 15 descriptions, since 0.1% or less of oxygen [a small amount of] is contained in inactive gas where inert gas replacement by inactive gas is carried out, electrode potential will be in a potential state which is balancing the minute amount oxygen, i.e., the range of 0.3-0.8V. From this, since electrode potential after stopping operation is manageable within suitable limits, catalyst de-activation can be controlled.

[0046]The invention according to claim 10 is characterized by an oxygen density in said inactive

gas being 0.005 to 0.05% in a stopping operation method of the fuel-cell-power-generation plant according to claim 9.

[0047]In the above inventions according to claim 10, where inert-gas-replacement operation by inactive gas is carried out, since an oxygen density in inactive gas is contained 0.001 to 0.1%, balanced maintenance of the electrode potential can be certainly carried out within the limits of 0.3-0.8V. From this, since electrode potential after stopping operation is maintainable within suitable limits, catalyst de-activation can be controlled.

[0048]

[Embodiment of the Invention]Below, the embodiment of a fuel-cell-power-generation plant by this invention, and starting and the stopping method for the same is concretely described with reference to Drawings. The same numerals are given to the same member as the conventional technology shown in drawing 7, and the explanation is omitted.

[0049](1) Describe below one embodiment which applied the 1st embodiment Claim 3 and the invention of 12 descriptions with reference to drawing 1 as a 1st embodiment.

[0050](Elements of the Invention) The composition of the fuel-cell-power-generation plant concerning this embodiment is explained first. That is, as shown in drawing 1, in addition to the inverter (inverter unit) 16 and the dummy resistor 17 which were connected via the inverter switch 18 and the dummy resistor switch 19, respectively, between the anode 2 and the cathode 3, the voltage detection circuits 20 are connected in parallel. And in the ac output line of the inverter 16. The electric power system 21 within a station which supplies a part of fuel cell output, and the external load system of 22 lines which supplies a fuel cell output outside are connected to electric power within a station in parallel, and via the within-a-station electric-power-system switch 23 and the external load system switch 24, it is connected, respectively so that opening and closing are possible.

[0051]The temperature sensor 25 which measures temperature to the inlet section of the cathode 3 of the single cell in the hot spot in the lamination single cell, for example, the lamination station most distant from the cold plate in a layer built cell, is arranged at the fuel cell body 1. In this case, the anode N_2 supplying system 9 and the cathode N_2 supplying system 13 are connected to anode 2 entrance and cathode 3 entrance like the conventional technology shown in drawing 7 via the anode N_2 supply valve 10 and the cathode N_2 supply valve 14.

[0052]A control device which has a control facility of various sorts in addition to the above composition

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[Translation done.]

OPERATION

(OPERATION) The operation of this embodiment which has the above composition is as follows. That is, when a stop command is inputted, the control device 26 orders it load reduction operation to the minimum load of electric power within a station with shift to a halt condition from a generating operation state. After the minimum load level attainment, while the control device 26 gives an opening signal to the external load system switch 24 and separates an external load system, it holds a closed signal to the within-a-station electric-power-system switch 23, and carries out idle mode operation by the minimum load level of only the electric power system 21 within a station.
[0054]In this case, since all the lamination single cells of the fuel cell body 1 are load levels with which it is satisfied of below a 0.8V/cell, catalyst de-activation accompanying sintering does not advance. Since it can be satisfied also with sufficiently small load (current density 10 mA/sq.cm grade) of cell voltage below 0.8V / cell if it is generally a plant of ordinary pressure operation, voltage control below 0.8V / cell by a within-a-station electric-power-system load value can be attained easily.
[0055]The control device 26 gives a temperature fall signal to the battery-cooling-water system 4 based on a stop command, and carries out temperature fall operation of the fuel cell body 1 in parallel to idle mode operation. In this case, the temperature sensor 25 detects continuously hot spot temperature of the fuel cell body 1 under idle mode operation, and continues transmitting a detection value to the control device 26.
[0056]And the detection values from the temperature sensor 25 are the range of 150-180 ** which is the idle mode shutdown temperature set up lower than operating temperature, and the stage which reached 150 ** desirably, The control device 26 gives a full-close signal to the fuel-supply-cutoff valve 7 and the air supply cutoff valve 11, and intercepts fuel and air supply at the same time it gives an opening signal to the within-a-station electric-power-system switch 23 and the inverter switch 18 and carries out fuel cell load shutdown. In parallel to this reactant gas supply interception control, further, the control device 26 gives an opening signal to the N_2 supply valves 10 and 14 of an anode inlet and a cathode inlet with an inactive gas supply control function, and carries out inert-gas-replacement operation by N_2 to the anode 2 and the cathode 3.
[0057]Although residual voltage occurs with remains H_2 rich gas of the anode 2, and the remains air of the cathode 3 at this time, this residual voltage is detected by the voltage detection circuits 20, and is transmitted to the control device 26, and inhibitory control of cell voltage is carried out. That is, when the detection value from the voltage detection circuits 20 exceeds a predetermined value, for example a 0.8V/cell is exceeded, the control device 26 gives an injection signal to the dummy resistor switch 19, forms the circuit by the dummy resistor 17, is consuming a cell output and controls cell voltage.
[0058]By the above operation, power generation stop operation of fuel cell body 1 self is completed (although the power generation operation to the external load system 22 has already stopped, power generation operation of fuel cell body 1 self is completed to this timing). The control device 26 continues the temperature fall operation of the fuel cell body 1 to a cell

storage temperature.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]The connection configuration figure showing the fuel-cell-power-generation plant concerning 1st and 3rd embodiments by this invention.
[Drawing 2]The graph which shows the relation of the catalyst surface reduction ratio and catalyst temperature accompanying sintering of a fuel cell catalyst.
[Drawing 3]The connection configuration figure showing the fuel-cell-power-generation plant concerning 2nd and 4th embodiments by this invention.
[Drawing 4]The connection configuration figure showing the fuel-cell-power-generation plant concerning a 5th embodiment by this invention.
[Drawing 5]The connection configuration figure showing the fuel-cell-power-generation plant concerning a 6th embodiment by this invention.
[Drawing 6]The graph which shows the relation between O_2 concentration and electrode potential.
[Drawing 7]The connection configuration figure showing an example of the conventional phosphoric acid fuel cell power generating plant.
[Drawing 8]The graph which shows the electrode potential under deactivation operation, and the relation of the amount of sag accompanying deactivation operation.
[Description of Notations]
1 -- Fuel cell body
2 -- Anode
3 -- Cathode
4 -- Battery-cooling-water system
5 -- Fuel reformer
6 -- Reformer burner
7 -- Fuel-supply-cutoff valve
8 -- Steam feed route
9 -- Anode N_2 supplying system
10 -- Anode N_2 supply valve
11 -- Air supply cutoff valve
12 -- Blower
13 -- Cathode N_2 supplying system
14 -- Cathode N_2 supply valve
15 -- Flueing course
16 -- Inverter
17 -- Dummy resistor
18 -- Inverter switch
19 -- Dummy resistor switch
20 -- Voltage detection circuits
21 -- Electric power system within a station

22 -- External load system
23 -- Within-a-station electric-power-system switch
24 -- External load system switch
25, 27 -- Temperature sensor
26 -- Control device
28 -- Minute amount H_2 content N_2 supply valve
29 -- Minute amount H_2 content N_2 supplying system
30 -- Cathode aeration regulating valve
31 -- Cathode air supply system

[Translation done.]

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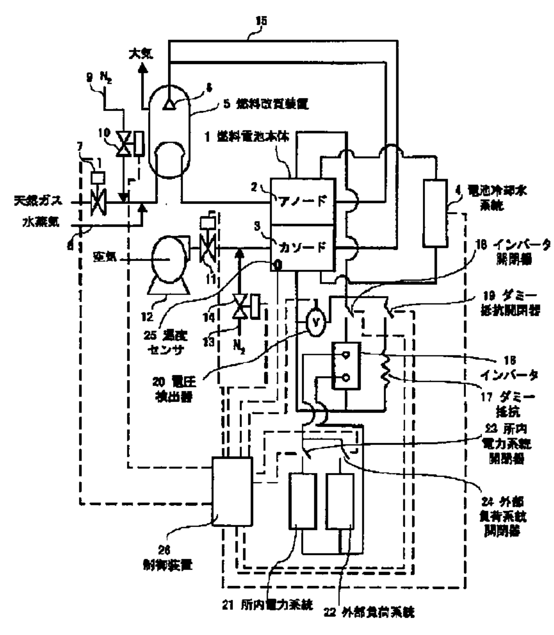
(54)【発明の名称】　燃料電池発電プラントおよびその起動・停止操作方法

(57)【要約】

【課題】　起動操作時や停止操作時における触媒の劣化を防止して、電池特性を低下させることなく安定に維持することが可能な、優れた燃料電池発電プラントおよびその起動・停止操作方法を提供する。

【解決手段】　アノード２とカソード３との間には、インバータ開閉器１８およびダミー抵抗開閉器１９を介してそれぞれ接続されたインバータ１６とダミー抵抗１７に加えて、電圧検出器２０が並列に接続される。インバータ１６の交流出力ラインには、所内電力系統２１と外部負荷系統２２ラインとが並列に接続されており、それぞれ、所内電力系統開閉器２３および外部負荷系統開閉器２４を介して開閉可能に接続される。燃料電池本体１には、その積層単セルにおけるホットスポットに、温度を測定する温度センサ２５が配置される。電池冷却水系統４、各種の弁および開閉器は、制御装置２６によって制御される。



【特許請求の範囲】

【請求項１】　燃料極および酸化剤極からなる単位電池を複数積層してなる燃料電池本体と、この燃料電池本体に燃料および酸化剤をそれぞれ供給する燃料改質装置および酸化剤供給装置と、燃料電池本体の温度を制御する電池冷却系統と、燃料電池本体の出力端に接続される直交変換装置と、この直交変換装置と外部負荷系統を接続する外部負荷系統開閉器を備えた燃料電池発電プラントの起動・停止操作方法において、

燃料電池発電プラントの起動操作時と停止操作時のいずれか一方の操作時に、

前記外部負荷系統開閉器を開状態とする一方で燃料電池発電プラントの所内電力系統だけに前記燃料電池本体の出力を供給することで、所内電力系統だけの負荷に相当する最低負荷で運転するアイドルモード運転を実施するステップを備えたことを特徴とする燃料電池発電プラントの起動・停止操作方法。

【請求項２】　燃料電池発電プラントの停止操作時に、停止指令に基づいて発電負荷を制御して前記最低負荷まで低減させるステップと、

前記最低負荷到達後に、前記外部負荷系統開閉器を開放して前記アイドルモード運転を実施するステップと、

前記アイドルモード運転を実施するステップと並行して、前記電池冷却系統を制御して前記燃料電池本体の降温操作を実施するステップと、

前記燃料電池本体温度が作動温度より低く設定されたアイドルモード運転停止温度まで降温した時点で、前記アイドルモード運転を停止するステップと、

前記アイドルモード運転を停止するステップと並行して、ガス置換操作と残留電圧抑制操作を含む本体停止操作を実施するステップを備え、

前記ガス置換操作は、前記燃料改質装置および前記酸化剤供給装置から前記燃料電池本体への改質燃料および酸化剤の供給を遮断すると同時に燃料電池本体へ不活性ガスを供給して残留ガスを追い出す操作であり、

前記残留電圧抑制操作は、前記燃料電池本体の燃料極と酸化剤極との間にダミー抵抗を投入することで残留電圧を抑制する操作であることを特徴とする請求項１記載の燃料電池発電プラントの起動・停止操作方法。

【請求項３】　前記アイドルモード運転停止温度が、前記燃料電池本体内部の最高温度が１５０～１８０℃の範囲に達した場合の温度であることを特徴とする請求項２記載の燃料電池発電プラントの起動・停止操作方法。

【請求項４】　前記燃料電池本体の降温操作を実施するステップ中で、前記アイドルモード運転中の電池降温速度、およびアイドルモード運転後の前記本体停止操作から電池保管温度に至るまでの電池降温速度を５０℃／ｈ以下に維持するように、前記電池冷却系統を制御することを特徴とする請求項２記載の燃料電池発電プラントの起動・停止操作方法。

【請求項５】　燃料電池発電プラントの起動操作時に、起動指令に基づいて前記電池冷却系統を制御して前記燃料電池本体の昇温操作を実施するステップと、

前記燃料電池本体温度が作動温度より低く設定されたアイドルモード運転開始温度まで昇温した時点で、前記改質装置および前記酸化剤供給装置から前記燃料電池本体に対して改質燃料および酸化剤をそれぞれ供給して前記アイドルモード運転を実施するステップと、

前記燃料電池本体温度が作動温度に到達した時点で、前記外部負荷系統開閉器を投入し、前記外部負荷系統へ電力を出力する外部起動操作を実施するステップを備えたことを特徴とする請求項１記載の燃料電池発電プラントの起動・停止操作方法。

【請求項６】　前記アイドルモード運転開始温度は、１５０℃以上の温度であることを特徴とする請求項５記載の燃料電池発電プラントの起動操作方法。

【請求項７】　前記燃料電池本体の昇温操作を実施するステップ中で、電池保管温度から前記アイドルモード運転直前までの電池昇温速度、およびアイドルモード運転中の電池昇温速度を５０℃／ｈ以下に維持するように、前記電池冷却系統を制御することを特徴とする請求項５記載の燃料電池発電プラントの起動・停止操作方法。

【請求項８】　前記燃料電池本体の昇温操作を実施するステップ中で、

燃料電池本体温度が１００℃に到達する以前に、４％以下の微量の水素を含む不活性ガスを燃料電池本体の燃料極に供給して、

前記燃料電池本体の電池電圧が予め設定された電圧抑制開始電圧以上に達した時点で、前記燃料電池本体の燃料極と酸化剤極との間にダミー抵抗を投入することで残留電圧を抑制することを特徴とする請求項５記載の燃料電池発電プラントの起動・停止操作方法。

【請求項９】　燃料極および酸化剤極からなる単位電池を複数積層してなる燃料電池本体と、この燃料電池本体に燃料および酸化剤をそれぞれ供給する燃料改質装置および酸化剤供給装置と、燃料電池本体の温度を制御する電池冷却系統と、燃料電池本体の出力端に接続される直交変換装置と、この直交変換装置と外部負荷系統を接続する外部負荷系統開閉器を備えた燃料電池発電プラントの停止操作を実施するために、前記燃料改質装置および前記酸化剤供給装置から前記燃料電池本体への改質燃料および酸化剤の供給を遮断すると同時に燃料電池本体へ不活性ガスを供給して残留ガスを追い出すガス置換操作と、前記燃料電池本体の燃料極と酸化剤極との間にダミー抵抗を投入することで残留電圧を抑制する残留電圧抑制操作を含む本体停止操作を実施するステップを備えた燃料電池発電プラントの停止操作方法において、

前記燃料電池本体の少なくとも燃料極または酸化剤極のどちらか一方に供給される前記不活性ガスが０．１％以下の微量の酸素を含むことを特徴とする燃料電池発電プ

ラントの停止操作方法。

【請求項１０】　前記不活性ガス中の酸素濃度が、０．００５～０．０５％であることを特徴とする請求項９記載の燃料電池発電プラントの停止操作方法。

【請求項１１】　燃料極および酸化剤極からなる単位電池を複数積層してなる燃料電池本体と、この燃料電池本体に燃料および酸化剤をそれぞれ供給する燃料改質装置および酸化剤供給装置と、燃料電池本体の温度を制御する電池冷却系統と、燃料電池本体の出力端に接続される直交変換装置と、この直交変換装置と外部負荷系統を接続する外部負荷系統開閉器を備えた燃料電池発電プラントにおいて、

前記外部負荷系統開閉器を制御する制御手段を備え、

前記制御手段によって、前記外部負荷系統開閉器を開状態とする一方で燃料電池発電プラントの所内電力系統だけに前記燃料電池本体の出力を供給することで、所内電力系統だけの負荷に相当する最低負荷で運転するアイドルモード運転を実施可能に構成されたことを特徴とする燃料電池発電プラント。

【請求項１２】　前記燃料電池本体に不活性ガスを供給する不活性ガス供給装置が設けられると共に、前記燃料電池本体の燃料極と酸化剤極の間に接続可能なダミー抵抗が設けられ、

前記制御手段は、

燃料電池発電プラントの停止操作時において、

停止指令に基づいて発電負荷を制御して前記最低負荷まで低減させ、

前記最低負荷到達後に、前記外部負荷系統開閉器を開放して前記アイドルモード運転を実施すると同時に、前記電池冷却系統を制御して前記燃料電池本体の降温操作を実施し、

前記燃料電池本体温度が作動温度より低く設定されたアイドルモード運転停止温度まで降温した時点で、前記アイドルモード運転を停止し、ガス置換操作と残留電圧抑制操作を含む本体停止操作を実施するように構成され、

前記ガス置換操作は、前記燃料改質装置および前記酸化剤供給装置から前記燃料電池本体への改質燃料および酸化剤の供給を遮断すると同時に前記不活性ガス供給装置から燃料電池本体へ不活性ガスを供給して残留ガスを追い出す操作であり、

前記残留電圧抑制操作は、前記燃料電池本体の燃料極と酸化剤極との間に前記ダミー抵抗を投入することで残留電圧を抑制する操作であることを特徴とする請求項１２記載の燃料電池発電プラント。

【請求項１３】　前記制御手段は、

燃料電池発電プラントの起動操作時において、

起動指令に基づいて前記電池冷却系統を制御して前記燃料電池本体の昇温操作を実施し、

前記燃料電池本体温度が作動温度より低く設定されたアイドルモード運転開始温度まで昇温した時点で、前記改質装置および前記酸化剤供給装置から前記燃料電池本体に対して改質燃料および酸化剤をそれぞれ供給して前記アイドルモード運転を実施し、

前記燃料電池本体温度が作動温度に到達した時点で、前記外部負荷系統開閉器を投入し、前記外部負荷系統へ電力を出力する外部起動操作を実施するように構成されたことを特徴とする請求項１１記載の燃料電池発電プラント。

【請求項１４】　前記燃料電池本体の燃料極に４％以下の微量の水素を含む不活性ガスを供給する微量水素含有ガス供給装置が設けられると共に、前記燃料電池本体の燃料極と酸化剤極の間に接続可能なダミー抵抗が設けられ、

前記制御手段は、

前記燃料電池発電プラントの前記起動操作時における前記燃料電池本体の前記昇温操作時において、

燃料電池本体温度が１００℃に到達する以前のタイミングで、前記微量水素含有ガス供給装置から前記微量の水素を含む不活性ガスを燃料電池本体の燃料極に供給して、

前記燃料電池本体の電池電圧が予め設定された電圧抑制開始電圧以上に達した時点で、前記燃料電池本体の燃料極と酸化剤極との間に前記ダミー抵抗を投入することで残留電圧を抑制することを特徴とする請求項１３記載の燃料電池発電プラント。

【請求項１５】　燃料極および酸化剤極からなる単位電池を複数積層してなる燃料電池本体と、この燃料電池本体に燃料および酸化剤をそれぞれ供給する燃料改質装置および酸化剤供給装置と、燃料電池本体に不活性ガスを供給する不活性ガス供給装置と、燃料電池本体の温度を制御する電池冷却系統と、燃料電池本体の出力端に接続される直交変換装置と、この直交変換装置と外部負荷系統を接続する外部負荷系統開閉器と、燃料電池本体の燃料極と酸化剤極との間に接続可能なダミー抵抗を備え、停止操作時には、前記燃料改質装置および前記酸化剤供給装置から前記燃料電池本体への改質燃料および酸化剤の供給を遮断すると同時に前記不活性ガス供給装置から燃料電池本体へ不活性ガスを供給して残留ガスを追い出すガス置換操作と、前記燃料電池本体の出力端に前記ダミー抵抗を投入することで残留電圧を抑制する残留電圧抑制操作を含む本体停止操作を実施するように構成された燃料電池発電プラントにおいて、

前記不活性ガス供給装置から前記燃料電池本体の少なくとも燃料極または酸化剤極のどちらか一方に供給される前記不活性ガスが０．１％以下の微量の酸素を含むことを特徴とする燃料電池発電プラント。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、燃料電池の起動停止操作における電池本体昇降温制御と起動および停止タ

イミングに改良を施した燃料電池発電プラントおよびその起動・停止操作方法に関する。

【０００２】

【従来の技術】燃料電池は、天然ガスを改質して得られる水素と、空気中の酸素とを電気化学的に反応させて直接発電する発電装置であり、小規模でも発電効率および総合エネルギー効率が高く、環境調和性に優れているという特徴を有する。かかる燃料電池は、電解質とこれを挟持する電極のアノードおよびカソードからなる単位電池を複数積層することによって構成されているが、中でも現在最も開発が進んでいるのは、電解質としてリン酸を使用したリン酸型燃料電池である。

【０００３】このようなリン酸型燃料電池を使用した燃料電池発電プラントの一例を、図７に従って以下に説明する。まず、燃料電池本体１の単位電池は、その背面に水素H_2 等の燃料が接触するアノード２と、その背面に酸素O_2 等の酸化剤が接触するカソード３とが、リン酸を含浸した保持体であるマトリックス（図示せず）を挟んでその両側に配置されることによって構成されている。電極であるアノード２およびカソード３は、多孔質炭素板の片面に白金等の触媒を塗布することにより作成されている。

【０００４】この場合、図中では一対のアノード２とカソード３のみが模式的に示されているが、実際には、このようなアノード２とカソード３からなる単位電池がガス分離板であるセパレータを介して交互に複数個積層されることによって、燃料電池本体１が構成されている。また、アノード２とセパレータとの間およびカソードとセパレータとの間には、前述したような燃料や酸化剤を流すためのガス流通用溝が形成されている。なお、かかる燃料電池本体の温度は、冷却水を供給する電池冷却水系統４によって所定値に制御される構成になっている。

【０００５】この燃料電池本体１におけるアノード２への燃料供給経路には、燃料改質装置５が接続されている。燃料改質装置５は、改質触媒を備え、この改質触媒に炭化水素を含む天然ガスを流通させて改質反応により水素リッチガスに改質する装置であり、加温用の改質器バーナ６を有すると共に、燃料供給遮断弁７を介して天然ガスを供給される構成となっている。また、燃料供給遮断弁７と燃料改質装置５との間の天然ガス供給経路には、水蒸気を供給する水蒸気供給経路８が接続されると共に、窒素N_2 を供給するアノードN_2 供給系統９が接続されている。このアノードN_2 供給系統９には、アノードN_2 供給弁１０が設けられている。

【０００６】一方、カソード３への酸化剤供給系統には、空気供給遮断弁１１を介してブロワ１２が接続されている。ここで、空気供給遮断弁１１とカソード３との間の空気供給経路には、窒素N_2 を供給するためのカソードN_2 供給系統１３が接続されている。このカソードN_2 供給系統１３には、カソードN_2 供給弁１４が設けられている。

【０００７】また、燃料電池本体１におけるアノード２およびカソード３のガス排気経路１５は、改質器バーナ６に接続されている。さらに、この燃料電池発電プラントでは、両電極間に、インバータ１６およびダミー抵抗１７が並列に接続されており、それぞれ、インバータ開閉器１８およびダミー抵抗開閉器１９を介して開閉可能に接続されている。

【０００８】以上のようなリン酸型燃料電池の発電プラントの作用は以下の通りである。まず、燃料電池本体１は、その内部で化学反応、電気化学反応を行う部分があるので、起動する前にそのような反応部分の温度を昇温して反応の許容温度範囲にすることが必要となる。この昇温作業は、燃料電池本体の温度制御を行う電池冷却水系統の冷却水温度を上昇することによって実施される。

【０００９】次に、燃料改質装置５に天然ガスと水蒸気との混合ガスが供給され、水蒸気改質反応によって、H_2 リッチガスが生成される。このH_2 リッチガスは、アノード２に供給される。一方、カソード３には、ブロワ１２によって圧縮された空気が供給される。そして、このようにアノード２に供給されたH_2 リッチガスとカソード３に供給された圧縮空気とが電気化学的に反応して、空気、水、および熱が生成される。アノード２およびカソード３から排出されるガスは、ガス排気経路１５を介して改質器バーナ６に供給され、燃焼後、大気中に放出される。

【００１０】また、発電停止操作においては、発電運転中に供給されたアノード２のH_2 リッチガスおよびカソード３の空気がそれぞれ残留しているため、不活性ガスである窒素N_2 を供給することにより、残留H_2 リッチガスおよび残留空気を追い出すパージ操作が行われる。すなわち、発電停止指令に従って、燃料供給遮断弁７と空気供給遮断弁１１を閉じて、アノード側へのH_2 リッチガスおよびカソード側への空気の供給を遮断する。これと同時に、アノードN_2 供給弁１０およびカソード供給弁１４を開き、アノードおよびカソード３に窒素N_2 を供給する。すると、アノード２およびカソード３に残留していたH_2 リッチガスおよび空気が窒素N_2 によって追い出される。

【００１１】ところで、以上のようなリン酸型燃料電池においては、高温状態で単位電池あたりの電池電圧が０．８Ｖ以上に維持されると、電極表面の貴金属触媒が溶出あるいは粗大化して活性面積が減少するシンタリング現象が発生することが知られており、このようなシンタリング現象は、電池特性を低下させる。また、単位電池あたりの電池電圧が０Ｖ以下となる転極現象が生じた場合には、電池材料の分解が生じ、電池に大きな損傷を与える。このため、発電中ばかりではなく、起動・停止操作中においても電池電圧の管理が必要になる。

【００１２】さらに、起動・停止操作中、特に停止操作

においては、上述の残留H_2 リッチガスおよび空気のパージが行われると共に、電池電圧抑制制御が施される。すなわち、インバータ１６は、発電停止指令に従ってＡＣ出力を低減させ、インバータ１６の運転不可能になる微小出力にまで低減したところで、インバータ開閉器１８およびダミー抵抗開閉器１９を切り替えて、ダミー抵抗１７を投入する。

【００１３】ダミー抵抗１７は、任意電圧、例えば０．８Ｖ／セル以上で投入され、０．５Ｖ／セル以下で開放されるように制御される。このダミー抵抗１７とアノード２およびカソード３に対する窒素N_2 パージ操作により電池電圧は抑制され、停止中の電池電圧の管理は完了する。

【００１４】

【発明が解決しようとする課題】しかしながら、以上のようなリン酸型燃料電池発電プラントにおいては、その停止操作および起動操作時に触媒が劣化して電池特性が低下するという問題点がある。この点について次に説明する。

【００１５】まず、リン酸型燃料電池発電プラントの停止操作においては、発電運転中に供給されたアノード２のH_2 リッチガスおよびカソード３の空気を不活性ガスを供給してガス置換する場合に、置換の遅れ時間が単セル間で異なり、また一つの単セルでもその主面中の位置によって異なる。そのために、置換遅れの小さい単セルまたは単セル中のそのような部分では単セル電圧が速やかに低下するのに対して、置換遅れの大きい単セルまたは単セル中のそのような部分では、残留反応ガスであるH_2 リッチガスおよび空気の電気化学エネルギーが、ダミー抵抗１７に吸収されるのに時間がかかるため、単セル電圧の低下にも時間がかかる。すなわち、置換遅れの大きい単セルまたは単セル中のそのような部分では、リッチガスおよび空気の電気化学エネルギーがダミー抵抗１７に吸収されるまでの間中、高い発生電位、例えば、０．８Ｖ以上にさらされることになる。

【００１６】この場合、従来の停止方法においては、作動温度２００℃付近で運転中の電流を遮断すると同時にガス置換を実施しているので、置換遅れの大きい単セルの電極触媒層は、作動温度に近い高温（２００℃付近）と高電位（０．８Ｖ／セル以上）にさらされることになる。

【００１７】電極触媒層がこのように、高温かつ高電位にさらされると、前述したように、貴金属触媒が溶出あるいは粗大化するいわゆるシンタリング現象が発生するため、電極触媒の有効反応面積が運転停止のたびに徐々に減少して、電極触媒の劣化が促進されてしまう。その結果、発電運転時の出力特性である電圧－電流特性の低下が促進され、燃料電池の寿命に悪影響を及ぼすという事態が発生する。またダミー抵抗１７は積層燃料電池をマクロに見て抵抗値が決められているので、局部的に残留する単セル電圧の上昇を抑制するに至らない場合が多い。

【００１８】一方、リン酸型燃料電池プラントの起動操作においては、燃料電池停止後の保管中に、ガス排気経路１５を介して、大気中のO_2 がアノード２およびカソード３内へ拡散侵入し、アノード２およびカソード３の触媒に吸着することにより、例えば、０．８Ｖ以上といった所定値以上の高い電位に維持されることになる。

【００１９】この状態で起動操作に伴う昇温が行われれば、高温状態で高電位（＞０．８Ｖ／セル）が維持されるため、触媒のシンタリング現象が進行し、触媒活性面積減少により電池特性の低下につながる。この場合、起動操作中にアノード２およびカソード３に、ほぼ同程度のO_2 濃度が滞留しているため、アノード２およびカソード３は同様の高電位に保持される。また、両者の電位差である電池電圧は、所定の電圧値を見掛け上満足しているので、電圧抑制操作であるダミー抵抗１７投入制御は実施されない。

【００２０】一方、発明者らの実験によれば、図８に示すように、起動停止操作中の電極電位が０．３Ｖから０．８Ｖの範囲を外れると、その起動停止操作に伴い電池電圧が下がり、燃料電池の性能が低下するという結果が得られている。これより、起動停止操作中も電極電池は０．３Ｖを下限電位とし、Ｏ．８Ｖを上限電位として、その間を電極電位の許容範囲としている。しかしながら、前述したように不活性ガス置換の時間遅れに伴いミクロ的に見た場合、現在のガス置換方法と燃料電池本体全体の電圧を感知してダミー抵抗を投入／開放するマクロ的制御によって、単セルまたは局部的に上限電位だけでなく下限電位をも満足することは極めて困難である。

【００２１】さらに、起動停止時の昇温および降温操作において、その温度変化が早い場合には、燃料電池本体内のリン酸体積が急変することにより、多孔質体からなる燃料電池積層部材からのリン酸の漏洩、または部材間におけるリン酸移動等により、電池本体設計で決められた燃料電池積層部材間のリン酸保持バランスを崩してしまい、電池寿命に悪影響を及ぼす現象も懸念されている。

【００２２】本発明は、以上のような従来技術の問題点を解決するために提案されたものであり、その目的は、起動操作時や停止操作時における触媒の劣化を防止して、電池特性を低下させることなく安定に維持することが可能な、優れた燃料電池発電プラントおよびその起動・停止操作方法を提供することである。

【００２３】

【課題を解決するための手段】上記の目的を達成するために、請求項１記載の発明は、燃料極および酸化剤極からなる単位電池を複数積層してなる燃料電池本体と、この燃料電池本体に燃料および酸化剤をそれぞれ供給する

燃料改質装置および酸化剤供給装置と、燃料電池本体の温度を制御する電池冷却系統と、燃料電池本体の出力端に接続される直交変換装置と、この直交変換装置と外部負荷系統を接続する外部負荷系統開閉器を備えた燃料電池発電プラントの起動・停止操作方法において、燃料電池発電プラントの起動操作時と停止操作時のいずれか一方の操作時に、アイドルモード運転を実施するステップを備えたことを特徴としている。ここで、アイドルモード運転は、前記外部負荷系統開閉器を開状態とする一方で燃料電池発電プラントの所内電力系統だけに前記燃料電池本体の出力を供給することで、所内電力系統だけの負荷に相当する最低負荷で運転するものである。

【００２４】また、請求項１１記載の発明は、燃料極および酸化剤極からなる単位電池を複数積層してなる燃料電池本体と、この燃料電池本体に燃料および酸化剤をそれぞれ供給する燃料改質装置および酸化剤供給装置と、燃料電池本体の温度を制御する電池冷却系統と、燃料電池本体の出力端に接続される直交変換装置と、この直交変換装置と外部負荷系統を接続する外部負荷系統開閉器を備えた燃料電池発電プラントにおいて、請求項１記載の方法を実施するための制御手段を備えたことを特徴とする燃料電池発電プラントである。

【００２５】以上のような請求項１、１１記載の発明では、発電運転停止後または発電運転開始前において、外部負荷と遮断した燃料電池プラント所内電力系だけの最低負荷でアイドルモード運転を実施することで、燃料電池本体内の全てのセルを上限電圧、例えば０．８Ｖ／セル以下に抑制した状態で、電池冷却水系を独立制御し、昇温操作または降温操作に移行することができる。これより、発電運転停止直後または発電運転開始前において、電極触媒層が高温かつ高電位にさらされることがないため、触媒劣化に至ることなく、外部負荷との遮断または外部負荷への移行をスムーズに実施することができる。

【００２６】請求項２記載の発明は、請求項１記載の燃料電池発電プラントの起動・停止操作方法において、燃料電池発電プラントの停止操作時に、次のステップを備えたことを特徴としている。すなわち、停止指令に基づいて発電負荷を制御して前記最低負荷まで低減させるステップと、前記最低負荷到達後に、前記外部負荷系統開閉器を開放して前記アイドルモード運転を実施するステップと、前記アイドルモード運転を実施するステップと並行して、前記電池冷却系統を制御して前記燃料電池本体の降温操作を実施するステップを備える。また、前記燃料電池本体温度が作動温度より低く設定されたアイドルモード運転停止温度まで降温した時点で、前記アイドルモード運転を停止するステップと、前記アイドルモード運転を停止するステップと並行して、ガス置換操作と残留電圧抑制操作を含む本体停止操作を実施するステップを備える。ここで、前記ガス置換操作は、前記燃料改質装置および前記酸化剤供給装置から前記燃料電池本体への改質燃料および酸化剤の供給を遮断すると同時に燃料電池本体へ不活性ガスを供給して残留ガスを追い出す操作である。前記残留電圧抑制操作は、前記燃料電池本体の燃料極と酸化剤極との間にダミー抵抗を投入することで残留電圧を抑制する操作である。

【００２７】請求項１２記載の発明は、請求項１１記載の燃料電池発電プラントにおいて、前記燃料電池本体に不活性ガスを供給する不活性ガス供給装置が設けられると共に、前記燃料電池本体の燃料極と酸化剤極の間に接続可能なダミー抵抗が設けられ、前記制御手段が、これらの不活性ガス供給装置とダミー抵抗を使用して、請求項２記載の方法を実施可能に構成されたことを特徴とする燃料電池発電プラントである。

【００２８】以上のような請求項２、１２記載の発明では、発電運転停止後、外部負荷と遮断した燃料電池プラント所内電力系だけの最低負荷でアイドルモード運転を実施することで、燃料電池本体内の全てのセルを上限電圧、例えば０．８Ｖ／セル以下に抑制した状態で、電池冷却水系を独立制御して降温操作を実施することができる。そして、電池本体温度が作動温度より低い所定温度まで降温した時点で、アイドルモード運転を停止し、燃料および酸化剤の供給を遮断すると同時に不活性ガスによるガス置換操作を開始し、ダミー抵抗を投入することで残留電圧を抑制する停止操作を実施することができる。これより、アイドルモード運転中の燃料電池本体温度が高温に維持される間は、全ての単セル電圧が許容値を満足することが可能となる。さらには、単セルまたは局部的に上限電圧以上の電圧が発生した場合でも、既に電池本体温度が作動温度よりも低くなっているので、アイドルモード運転後の停止操作時のダミー抵抗の投入による残留電圧抑制操作によって触媒の劣化を抑制することができる。

【００２９】請求項３記載の発明は、請求項１記載の燃料電池発電プラントの起動・停止操作方法において、前記アイドルモード運転停止温度が、前記燃料電池本体内部の最高温度が１５０～１８０℃の範囲に達した場合の温度であることを特徴としている。

【００３０】以上のような請求項３記載の発明では、発電運転停止後、アイドルモード運転を実施することで、燃料電池本体内の全てのセルを上限電圧、例えば０．８Ｖ／セル以下に抑制した状態で、電池冷却水系を独立制御して降温操作を実施することができる。そして、電池最高温度が１５０～１８０℃にまで降温した時点で、アイドルモード運転を停止し、供給燃料および酸化剤を遮断すると同時に不活性ガスによるガス置換操作を開始し、ダミー抵抗を投入することで残留電圧を抑制する停止操作を実施することができる。これより、アイドルモード運転中の燃料電池本体温度が高温に維持される間は、全ての単セル電圧が許容値を満足することが可能と

なる。さらには、単セルまたは局部的に上限電圧以上の電圧が発生した場合でも、既に電池本体の最高温度が、触媒の劣化速度を十分に抑制できる温度領域１５０～１８０℃まで低減されているので、アイドルモード運転後の停止操作時のダミー抵抗の投入による残留電圧抑制操作によって、停止操作に伴う触媒劣化を十分に抑制することができる。

【００３１】請求項４記載の発明は、請求項２記載の燃料電池発電プラントの起動・停止操作方法において、前記燃料電池本体の降温操作を実施するステップ中で、前記アイドルモード運転中の電池降温速度、およびアイドルモード運転後の前記本体停止操作から電池保管温度に至るまでの電池降温速度を５０℃／ｈ以下に維持するように、前記電池冷却系統を制御することを特徴としている。

【００３２】以上のような請求項４記載の発明では、発電停止後のアイドルモード運転中およびその後の電池保管温度までの、一連の電池本体の降温操作において、その降温速度を５０℃／ｈ以下に制限したので、急激なリン酸体積変化を起こすことなく停止操作を完了することができる。これより、多孔質体からなる燃料電池積層部材からのリン酸の漏洩や部材間におけるリン酸移動等を回避することができるため、電池本体設計で決められた燃料電池積層部材間のリン酸保持バランスが崩れることを防止でき、優れた電池寿命を確保できる。

【００３３】請求項５記載の発明は、請求項１記載の燃料電池発電プラントの起動・停止操作方法において、燃料電池発電プラントの起動操作時に、次のステップを備えたことを特徴としている。すなわち、起動指令に基づいて前記電池冷却系統を制御して前記燃料電池本体の昇温操作を実施するステップと、前記燃料電池本体温度が作動温度より低く設定されたアイドルモード運転開始温度まで昇温した時点で、前記改質装置および前記酸化剤供給装置から前記燃料電池本体に対して改質燃料および酸化剤をそれぞれ供給して前記アイドルモード運転を実施するステップを備える。また、前記燃料電池本体温度が作動温度に到達した時点で、前記外部負荷系統開閉器を投入し、前記外部負荷系統へ電力を出力する外部起動操作を実施するステップを備える。

【００３４】請求項１３記載の発明は、請求項１１記載の燃料電池発電プラントにおいて、前記制御手段が、請求項５記載の方法を実施可能に構成されたことを特徴とする燃料電池発電プラントである。

【００３５】以上のような請求項５、１３記載の発明では、燃料電池保管中に電池内に大気中から混入した酸素により発生する高電位状態（０．８Ｖ以上）の電極が、触媒劣化が進行する高温状態にさらされる以前に、作動温度より低い温度でアイドルモード運転を開始することで、燃料電池本体内の全てのセルを上限電圧、例えば０．８Ｖ／セル以下に抑制することができる。これより、作動温度まで高電位状態にさらされる場合に比べて、触媒の劣化を抑制することができる。

【００３６】請求項６記載の発明は、請求項５記載の燃料電池発電プラントの起動・停止操作方法において、前記アイドルモード運転開始温度が、１５０℃以上の温度であることを特徴としている。

【００３７】以上のような請求項６記載の発明では、燃料電池保管中に電池内に大気中から混入した酸素により発生する高電位状態（０．８Ｖ以上）の電極が、触媒劣化が進行する高温状態にさらされる以前に、触媒劣化速度が未だ加速しない温度１５０℃に到達した段階で、アイドルモード運転を開始することで、燃料電池本体内の全てのセルを上限電圧、例えば０．８Ｖ／セル以下に抑制することができる。これより、起動操作に伴う触媒劣化を十分に抑制することができる。

【００３８】請求項７記載の発明は、請求項５記載の燃料電池発電プラントの起動・停止操作方法において、前記燃料電池本体の昇温操作を実施するステップ中で、電池保管温度から前記アイドルモード運転直前までの電池昇温速度、およびアイドルモード運転中の電池昇温速度を５０℃／ｈ以下に維持するように、前記電池冷却系統を制御することを特徴としている。

【００３９】以上のような請求項７記載の発明では、起動後の電池保管温度から前記アイドルモード運転直前までの電池昇温操作およびアイドルモード運転中の一連の電池本体昇温操作において、その昇温操作を５０℃／ｈ以下に制限したので、急激なリン酸体積変化を起こすことなく昇温操作を完了することができる。これより、多孔質体からなる燃料電池積層部材からのリン酸の漏洩や部材間におけるリン酸移動等を回避することができるため、電池本体設計で決められた燃料電池積層部材間のリン酸保持バランスが崩れることを防止でき、優れた電池寿命を確保できる。

【００４０】請求項８記載の発明は、請求項５記載の燃料電池発電プラントの起動・停止操作方法において、前記燃料電池本体の昇温操作を実施するステップ中で、燃料電池本体温度が１００℃に到達する以前に、４％以下の微量の水素を含む不活性ガスを燃料電池本体の燃料極に供給して、前記燃料電池本体の電池電圧が予め設定された電圧抑制開始電圧以上に達した時点で、前記燃料電池本体の燃料極と酸化剤極との間にダミー抵抗を投入することで残留電圧を抑制することを特徴としている。

【００４１】請求項１４記載の発明は、請求項１３記載の燃料電池発電プラントにおいて、前記燃料電池本体に不活性ガスを供給する不活性ガス供給装置が設けられると共に、前記燃料電池本体の燃料極と酸化剤極の間に接続可能なダミー抵抗が設けられ、前記制御手段が、これらの不活性ガス供給装置とダミー抵抗を使用して、請求項８記載の方法を実施可能に構成されたことを特徴とする燃料電池発電プラントである。

【００４２】以上のような請求項８、１４記載の発明では、燃料電池保管中に電池内の大気中から混入した酸素により発生する高電位状態（０．８Ｖ以上）の電極が、触媒劣化が進行する高温状態に到達する前に、燃料極に微量のH_2を供給することで、燃料極の電位を低減しかつ酸化剤極の電位を電圧値として観測することができる。そして、観測される電圧値が予め設定された電圧抑制開始電圧以上に達した場合に、ダミー抵抗を投入して酸化剤極中のO_2を消費することで、酸化剤極の電位を抑制することができる。これより、昇温に伴う高温、高電位状態で進行する触媒劣化を防止することができる。

【００４３】請求項９記載の発明は、燃料極および酸化剤極からなる単位電池を複数積層してなる燃料電池本体と、この燃料電池本体に燃料および酸化剤をそれぞれ供給する燃料改質装置および酸化剤供給装置と、燃料電池本体の温度を制御する電池冷却系統と、燃料電池本体の出力端に接続される直交変換装置と、この直交変換装置と外部負荷系統を接続する外部負荷系統開閉器を備えた燃料電池発電プラントの停止操作を実施するための燃料電池発電プラントの停止操作方法に関するものである。そして、特に、前記燃料改質装置および前記酸化剤供給装置から前記燃料電池本体への改質燃料および酸化剤の供給を遮断すると同時に燃料電池本体へ不活性ガスを供給して残留ガスを追い出すガス置換操作と、前記燃料電池本体の燃料極と酸化剤極との間にダミー抵抗を投入することで残留電圧を抑制する残留電圧抑制操作を含む本体停止操作を実施するステップを備えた燃料電池発電プラントの停止操作方法において、前記燃料電池本体の少なくとも燃料極または酸化剤極のどちらか一方に供給される前記不活性ガスが０．１％以下の微量の酸素を含むことを特徴としている。

【００４４】請求項１５記載の発明は、燃料極および酸化剤極からなる単位電池を複数積層してなる燃料電池本体と、この燃料電池本体に燃料および酸化剤をそれぞれ供給する燃料改質装置および酸化剤供給装置と、燃料電池本体に不活性ガスを供給する不活性ガス供給装置と、燃料電池本体の温度を制御する電池冷却系統と、燃料電池本体の出力端に接続される直交変換装置と、この直交変換装置と外部負荷系統を接続する外部負荷系統開閉器と、燃料電池本体の燃料極と酸化剤極の間に接続可能なダミー抵抗を備えた燃料電池発電プラントにおいて、前記不活性ガス供給装置から前記燃料電池本体の少なくとも燃料極または酸化剤極のどちらか一方に供給される前記不活性ガスが０．１％以下の微量の酸素を含むことを特徴としている。

【００４５】以上のような請求項９、１５記載の発明では、不活性ガスによるガス置換が実施された状態で、不活性ガス中に０．１％以下の微量の酸素が含まれているので、電極電位はその微量酸素に平衡となる電位状態、すなわち、０．３～０．８Ｖの範囲になる。これより、停止操作後の電極電位を、適切な範囲内に管理することができるので、触媒劣化を抑制できる。

【００４６】請求項１０記載の発明は、請求項９記載の燃料電池発電プラントの停止操作方法において、前記不活性ガス中の酸素濃度が、０．００５～０．０５％であることを特徴としている。

【００４７】以上のような請求項１０記載の発明では、不活性ガスによるガス置換操作が実施された状態で、不活性ガス中の酸素濃度が０．００１～０．１％含まれているので、電極電位を、０．３～０．８Ｖの範囲内に確実に平衡維持することができる。これより、停止操作後の電極電位を、適切な範囲内に維持することができるので、触媒劣化を抑制できる。

【００４８】

【発明の実施の形態】以下には、本発明による燃料電池発電プラントおよびその起動・停止方法の実施の形態を、図面を参照して具体的に説明する。なお、図７に示した従来技術と同一の部材には同一の符号を付してその説明を省略する。

【００４９】（１）第１の実施の形態

請求項３、１２記載の発明を適用した一つの実施の形態を、第１の実施の形態として、図１を参照して以下に説明する。

【００５０】（構成）まず、本実施の形態に係る燃料電池発電プラントの構成を説明する。すなわち、図１に示すように、アノード２とカソード３との間には、インバータ開閉器１８およびダミー抵抗開閉器１９を介してそれぞれ接続されたインバータ（直交変換装置）１６とダミー抵抗１７に加えて、電圧検出器２０が並列に接続されている。そして、インバータ１６の交流出力ラインには、所内電力に燃料電池出力の一部を供給する所内電力系統２１と外部に燃料電池出力を供給する外部負荷系統２２ラインとが並列に接続されており、それぞれ、所内電力系統開閉器２３および外部負荷系統開閉器２４を介して開閉可能に接続されている。

【００５１】また、燃料電池本体１には、その積層単セルにおけるホットスポット、例えば、積層電池内冷却板から最も離れた積層位置にある単セルのカソード３の入口部に、温度を測定する温度センサ２５が配置されている。この場合、アノード２入口およびカソード３入口には、図７に示した従来技術と同様に、アノードN_2供給弁１０およびカソードN_2供給弁１４を介してアノードN_2供給系統９およびカソードN_2供給系統１３が接続されている。

【００５２】さらに、以上の構成に加えて、多種類の制御機能を有する制御装置（制御手段）２６が設けられている。すなわち、制御装置２６は、温度センサ２５の検出値により、電池冷却水系統４に出力を与えることで電池温度を制御する電池温度制御機能、インバータ開閉器１８の開閉を制御するインバータ開閉制御機能、燃料供

給遮断弁７および空気供給遮断弁１１の開閉を制御する反応ガス供給制御機能、アノードN_2 供給弁１０およびカソードN_2 供給弁１４の開閉を制御する不活性ガス供給制御機能、電圧検出器２０の検出値より、ダミー抵抗開閉器１９の開閉を制御するダミー抵抗開閉制御機能、外部負荷系統２２および所内電力系統２１への投入／遮断を行う外部負荷系統開閉器２４および所内電力系統開閉器２３を制御する系統開閉制御機能、等を有する。

【００５３】（作用）以上のような構成を有する本実施の形態の作用は以下の通りである。すなわち、停止指令が入力された場合、発電運転状態から停止状態への移行に伴い、制御装置２６は、所内電力相当の最低負荷まで負荷低減操作を指令する。最低負荷レベル到達後、制御装置２６は、外部負荷系統開閉器２４に開信号を与えて外部負荷系統を切り離す一方で、所内電力系統開閉器２３に対しては閉信号を保持し、所内電力系統２１だけの最低負荷レベルによるアイドルモード運転を実施する。

【００５４】この場合、燃料電池本体１の全ての積層単セルは、０．８Ｖ／セル以下を満足する負荷レベルであるので、シンタリングに伴う触媒劣化は進行しない。一般的に常圧運転のプラントであれば、十分小さい負荷（電流密度１０ｍＡ／ｓｑ．ｃｍ程度）でも、０．８Ｖ／セル以下の電池電圧を満足することができるので、所内電力系統負荷値による０．８Ｖ／セル以下の電圧抑制は容易に達成できる。

【００５５】また、制御装置２６は、停止指令に基づいて、電池冷却水系統４に降温信号を与え、アイドルモード運転と並行して燃料電池本体１の降温操作を実施する。この場合、温度センサ２５は、アイドルモード運転中の燃料電池本体１のホットスポット温度を連続的に検出し、検出値を制御装置２６に送信し続ける。

【００５６】そして、温度センサ２５からの検出値が、作動温度より低く設定されたアイドルモード運転停止温度である１５０～１８０℃の範囲、望ましくは１５０℃に到達した段階で、制御装置２６は、所内電力系統開閉器２３およびインバータ開閉器１８に開信号を与え、燃料電池負荷遮断を実施すると同時に、燃料供給遮断弁７および空気供給遮断弁１１に全閉信号を与えて燃料および空気の供給を遮断する。制御装置２６は、この反応ガス供給遮断制御に並行してさらに、不活性ガス供給制御機能によってアノード入口およびカソード入口のN_2 供給弁１０，１４に開信号を与えて、アノード２およびカソード３に対し、N_2 によるガス置換操作を実施する。

【００５７】この時、アノード２の残留H_2 リッチガスおよびカソード３の残留空気により残留電圧が発生するが、この残留電圧は電圧検出器２０によって検出されて制御装置２６に送信され、電池電圧の抑制制御が実施される。すなわち、制御装置２６は、電圧検出器２０からの検出値が所定値を越えた場合、例えば０．８Ｖ／セルを越えた場合に、ダミー抵抗開閉器１９に投入信号を与えて、ダミー抵抗１７による回路を形成し、電池出力を消費することで、電池電圧の抑制を実施する。

【００５８】以上の操作により、燃料電池本体１自身の発電停止操作が完了する（外部負荷系統２２への発電操作は既に停止しているが、燃料電池本体１自身の発電操作はこのタイミングで完了する）。なお、制御装置２６は、電池保管温度まで燃料電池本体１の降温操作を継続する。

【００５９】（効果）以上のような本実施の形態の効果は以下の通りである。すなわち、停止指令に伴う外部負荷系統２２の遮断操作後も、燃料電池本体１はアイドルモード運転を実施することにより、積層単セル全てを、０．８Ｖ／セル以下の所定値に管理できる。そのため、シンタリングによる触媒劣化が進行することなく、燃料電池本体１の降温操作を良好に実施することができる。また、燃料電池本体１のホットスポット温度が１５０～１８０℃まで降温した段階で、アイドルモード運転を停止し、事実上の電池運転停止操作を実施するが、この場合のN_2 によるガス置換およびダミー抵抗１７によるマクロな電圧抑制操作では、積層単セルの一部に０．８Ｖ／セル以上の所定値を逸脱する現象が発生しても、既に燃料電池本体温度は所定の温度まで低下しているので、シンタリングによる触媒劣化の進行程度は鈍く、許容できる程度である。

【００６０】ここで、図２は、本発明者等が実験により求めた電池温度（触媒温度）とシンタリングの程度を表す触媒表面積現象比との関係を示すグラフであり、条件は、電極電位：０．９Ｖ、電位保持時間：１ｈである。この図２に示すように、低温ほどシンタリングに伴う触媒表面積減少比は大きく低減しており、１５０℃における触媒表面積減少比、すなわち、シンタリングの進行速度は、停止操作時間を考慮した場合にほとんど許容できる範囲にある。

【００６１】なお、燃料電池本体１のホットスポットが１５０℃より低い温度での停止操作は、シンタリングを抑制する上で十分効果的であるが、現実的には電池冷却水系統４から燃料改質装置５へ供給している水蒸気圧力の確保、および燃料電池本体１のコールドスポットでのリン酸を含む生成水の凝縮に伴う反応ガス拡散不良現象（低温領域で凝縮したリン酸が電極の反応ガス流通路を閉塞し、電池の電気化学反応を阻害する）により、プラント運転上の問題点および電池特性を低下させる問題点が生じることになる。

【００６２】したがって、本実施の形態のホットスポット温度１５０～１８０℃、特に１５０℃での実質的な燃料電池本体の負荷遮断操作は、ガス拡散不良に伴う特性低下を引き起こすことなく、触媒劣化進行を防止できる最も信頼性の高い燃料電池発電プラントの停止操作を提供することができるものであり、実用性が高い。

【００６３】（２）第２の実施の形態

請求項６、１３記載の発明を適用した一つの実施の形態を、第２の実施の形態として、図３を参照して以下に説明する。

【００６４】（構成）まず、本実施の形態に係る燃料電池発電プラントの構成を説明する。すなわち、図３に示すように、アノード２とカソード３との間に、インバータ開閉器１８およびダミー抵抗開閉器１９を介してそれぞれ接続されたインバータ１６とダミー抵抗１７に加えて、電圧検出器２０が並列に接続されている点は前記第１の実施の形態と同様である。そして、インバータ１６の交流出力ラインには、所内電力に燃料電池出力の一部を供給する所内電力系統２１と外部に燃料電池出力を供給する外部負荷系統２２ラインとが並列に接続され、それぞれ、所内電力系統開閉器２３および外部負荷系統開閉器２４を介して開閉可能に接続されている点も、前記第１の実施の形態と同様である。

【００６５】これに対して、燃料電池本体１に設けられる温度センサは、積層単セルにおけるホットスポットに限定して配置されるものではない。本実施の形態においては、よりマクロ的に燃料電池本体１の温度を測定するために、燃料電池本体１内の任意の位置に温度センサ２７が配置されている。

【００６６】さらに、本実施の形態の制御装置２６は、前記第１の実施の形態と同様の多種類の制御機能を有する。なお、本実施の形態で実際に必要な制御機能は、温度センサ２７の検出値により電池冷却水系統４に出力を与えることで電池温度を制御する電池温度制御機能、インバータ開閉器１８の開閉を制御するインバータ開閉制御機能、燃料供給遮断弁７および空気供給遮断弁１１の開閉を制御する反応ガス供給制御機能、外部負荷系統２２および所内電力系統２１への投入／遮断を行う外部負荷系統開閉器２４および所内電力系統開閉器２３を制御する系統開閉制御機能、等である。

【００６７】（作用）以上のような構成を有する本実施の形態の作用は以下の通りである。すなわち、起動指令が入力された場合、燃料電池保管状態から起動状態への移行に伴い、制御装置２６は、電池冷却水系統４に昇温信号を与えて燃料電池本体１の昇温操作を実施する。この場合、温度センサ２７は、燃料電池本体１の温度を連続的に検出し、検出値を制御装置２６に送信し続ける。

【００６８】そして、温度センサ２７からの検出値、すなわち、燃料電池本体１の温度が１５０℃に到達した場合、制御装置２６は、アイドルモード運転への移行を実施する。すなわち、燃料供給遮断弁７の開操作により燃料改質装置５からアノード２へH_2 リッチガスを導入し、その後、空気供給遮断弁１１の開操作によりカソード３への空気の供給を行う。さらには、燃料電池本体１の発生電圧を電圧検出器２０にて検知し、検出値が所定値に到達した段階、例えば０．８Ｖ／セルに達した段階で、インバータ開閉器１８を投入し、かつ所内電力系統開閉器２３も投入することによって、所内電力系統２１ラインを形成し、アイドルモード運転への負荷移行を完了する。

【００６９】制御装置２６は、このアイドルモード運転と燃料電池本体１の昇温操作を並行して継続する。そして、燃料電池本体１の温度が所定の作動温度、例えば１９０℃に到達した時点で、制御装置２６は、外部負荷系統開閉器２４を投入し、外部負荷系統２２ラインを形成して、アイドルモード運転からの負荷上昇制御を実施する。所定の外部負荷値に到達した段階で発電運転モードに移行し、一連の起動操作が完了する。

【００７０】（効果）以上のような本実施の形態の効果は以下の通りである。すなわち、起動操作の開始にあたり、燃料電池保管中に電池内に大気中から混入した酸素により発生する高電位状態（０．８Ｖ以上）の電極は、昇温操作に伴い高温状態に移行するが、これに対して、シンタリングによる触媒劣化進行速度が未だ許容できる温度、すなわち１５０℃に到達した時点でアイドルモード運転を開始することで、燃料電池本体内の全てのセルを上限電圧、０．８Ｖ／セル以下に抑制することができる。

【００７１】これに関して、前記第１の実施の形態について述べたように、本発明者等の実験結果によれば、比較的低温の１５０℃での高電位状態においては、作動温度、例えば２００℃程度に比べて、シンタリングの進行速度は大きく低減し、起動操作時間を考慮した場合に、ほとんど許容できる範囲である。

【００７２】また、同じく前記第１の実施の形態について述べたように、１５０℃より低い温度でのアイドルモード運転は、シンタリングを抑制する上で十分効果的であるが、現実的には電池冷却水系統４から燃料改質装置５へ供給している水蒸気圧力の確保、および燃料電池本体１のコールドスポットでのリン酸を含む生成水の凝縮に伴う反応ガス拡散不良現象により、プラント運転上の問題点および電池特性を低下させる問題点が生じることになる。

【００７３】したがって、本実施の形態に示すような燃料電池温度１５０℃以上での実質的な燃料電池本体の負荷移行操作は、ガス拡散不良に伴う特性低下を引き起こすことなく、触媒劣化進行を防止できる最も信頼性の高い燃料電池発電プラントの起動操作を提供することができるものであり、実用性が高い。

【００７４】（３）第３の実施の形態

請求項４記載の発明を適用した一つの実施の形態を、第３の実施の形態として以下に説明する。

【００７５】（構成）まず、本実施の形態に係る燃料電池発電プラントは、図１に示した前記第１の実施の形態において、制御装置２６が、さらに、電池冷却水温度の降温速度が５０℃／ｈ以下になるように電池冷却水系統４を制御する機能をも有することを特徴としている。な

お、他の部分については、前記第１の実施の形態と全く同様に構成されている。

【００７６】（作用）以上のような構成を有する本実施の形態の作用を以下に説明する。すなわち、停止指令が入力された場合、発電運転状態から停止状態への移行に伴い、制御装置２６は、所内電力相当の最低負荷まで負荷低減操作を指令する。最低負荷レベル到達後、制御装置２６は、外部負荷系統開閉器２４に開信号を与えて外部負荷系統を切り離す一方で、所内電力系統開閉器２３に対しては閉信号を保持し、所内電力系統２１だけの最低負荷レベルによるアイドルモード運転を実施する。

【００７７】また、制御装置２６は、停止指令に基づいて、電池冷却水系統４に降温信号を与え、アイドルモード運転と並行して、冷却水の降温速度が５０℃／ｈ以下を維持するようにして燃料電池本体１の降温操作を実施する。この場合、温度センサ２５は、燃料電池本体１の温度を連続的に検出し、検出値を制御装置２６に送信し続ける。

【００７８】そして、温度センサ２５からの検出値が、１５０～１８０℃の範囲、望ましくは１５０℃に到達した段階で、制御装置２６は、所内電力系統開閉器２３およびインバータ開閉器１８に開信号を与え、燃料電池負荷遮断を実施すると同時に、燃料供給遮断弁７および空気供給遮断弁１１に全閉信号を与えて燃料および空気の供給を遮断する。制御装置２６は、この反応ガス供給遮断制御に並行してさらに、不活性ガス供給制御機能によってアノード入口およびカソード入口のN_2供給弁１０，１４に開信号を与えて、アノード２およびカソード３に対し、N_2によるガス置換操作を実施する。

【００７９】この時、アノード２の残留H_2リッチガス及びカソード３の残留空気により残留電圧が発生するが、この残留電圧は電圧検出器２０によって検出されて制御装置２６に送信され、電池電圧の抑制制御が実施される。すなわち、制御装置２６は、電圧検出器２０からの検出値が所定値を越えた場合、例えば０．８Ｖ／セルを越えた場合に、ダミー抵抗開閉器１９に投入信号を与えて、ダミー抵抗１７による回路を形成し、電池出力を消費することで、電池電圧の抑制が実施される。以上の操作により、燃料電池本体１自身の発電停止操作は完了するが、制御装置２６は、アイドルモード運転中の降温速度だけでなく、アイドルモード後の発電停止操作から電池保管温度までの降温速度が５０℃／ｈ以下を維持するように制御しながら、電池冷却水系統４の降温操作を継続する。

【００８０】（効果）以上のような本実施の形態によれば、前記第１の実施の形態の効果に加えて、さらに以下のような効果が得られる。すなわち、発電停止後のアイドルモード運転中およびその後の電池保管温度までの一連の電池本体の降温操作において、その降温速度を５０℃／ｈ以下に制限することにより、急激なリン酸体積変化を起こすことなく停止操作を完了することができる。

【００８１】したがって、多孔質体からなる燃料電池積層部材からのリン酸の漏洩や部材間におけるリン酸移動等を回避することができるため、電池本体設計で決められた燃料電池積層部材間のリン酸保持バランスが崩れることを防止でき、優れた電池寿命を確保することができる。

【００８２】（４）第４の実施の形態

請求項７記載の発明を適用した一つの実施の形態を、第４の実施の形態として以下に説明する。

【００８３】（構成）まず、本実施の形態に係る燃料電池発電プラントは、図３に示した前記第２の実施の形態において、制御装置２６が、さらに、電池冷却水温度の昇温速度が５０℃／ｈ以下になるように電池冷却水系統４を制御する機能をも有することを特徴としている。なお、他の部分については、前記第２の実施の形態と全く同様に構成されている。

【００８４】（作用）以上のような構成を有する本実施の形態の作用を以下に説明する。すなわち、起動指令が入力された場合、燃料電池保管状態から起動状態への移行に伴い、制御装置２６は、電池冷却水系統４に昇温信号を与えて燃料電池本体１の昇温操作を実施する。この場合、制御装置２６は、冷却水の昇温速度が５０℃／ｈ以下を維持するようにして、燃料電池本体１の昇温操作を実施する。この場合、温度センサ２７は、燃料電池本体１の温度を連続的に検出し、検出値を制御装置２６に送信し続ける。

【００８５】そして、温度センサ２７からの検出値、すなわち、燃料電池本体１の温度が１５０℃に到達した場合、制御装置２６は、アイドルモード運転への移行を実施する。なお、制御装置２６は、このアイドルモード運転と電池本体１の昇温操作を並行して継続し、電池保管温度からアイドルモード運転直前までの電池昇温速度と同様に、アイドルモード運転中の電池昇温速度が５０℃／ｈ以下を満足するように電池冷却水系統４の昇温操作を実施する。

【００８６】次に、燃料電池本体１の温度が所定の作動温度、例えば１９０℃に到達した時点で、制御装置２６は、外部負荷系統開閉器２４を投入し、外部負荷系統２２ラインを形成して、アイドルモード運転からの負荷上昇制御を実施する。所定の外部負荷値に到達した段階で発電運転モードに移行し、一連の起動操作が完了する。

【００８７】（効果）以上のような本実施の形態によれば、前記第２の実施の形態の効果に加えて、さらに以下のような効果が得られる。すなわち、起動後の電池保管温度から前記アイドルモード運転直前までの電池昇温操作およびアイドルモード運転中の一連の電池本体昇温操作において、その昇温操作を５０℃／ｈ以下に制限することにより、急激なリン酸体積変化を起こすことなく昇温操作を完了することができる。

【００８８】したがって、多孔質体からなる燃料電池積層部材からのリン酸の漏洩や部材間におけるリン酸移動等を回避することができるため、電池本体設計で決められた燃料電池積層部材間のリン酸保持バランスが崩れることを防止でき、優れた電池寿命を確保することができる。

【００８９】（５）第５の実施の形態

請求項８、１４記載の発明を適用した一つの実施の形態を、第５の実施の形態として図４を参照して以下に説明する。

【００９０】（構成）まず、本実施の形態に係る燃料電池発電プラントの構成は、図３に示した前記第２の実施の形態において、さらに、微量水素含有窒素を供給するための構成を追加したものである。すなわち、アノード２の入口には、微量H_2 含有N_2 供給弁２８を介して、４％以下の微量のH_2 を含む微量H_2 含有N_2 供給系統（微量水素含有ガス供給装置）２９が接続されている。なお、他の部分については、前記第２の実施の形態と全く同様に構成されている。

【００９１】（作用）以上のような構成を有する本実施の形態の作用は以下の通りである。すなわち、起動指令が入力された場合、燃料電池保管状態から起動状態への移行に伴い、制御装置２６は電池冷却水系統４に昇温信号を与えて燃料電池本体１の昇温操作を実施する。この場合、温度センサ２７は、燃料電池本体１の温度を連続的に検出し、検出値を制御装置２６に送信し続ける。

【００９２】そして、燃料電池本体１の温度が１００℃に到達する以前に、制御装置２６は、アノード微量H_2 含有N_2 供給弁２８に開信号を与え、微量H_2 含有N_2 供給系統２９からアノード２に対して、４％以下の微量のH_2 を含むN_2 ガスが供給される。この時点で、アノード２中には、電池保管中空気が侵入している可能性があるので、高濃度のH_2 を供給した場合には爆発の危険性があるが、本実施の形態でアノード２に供給されるN_2 ガス中のH_2 濃度は、４％以下の爆発限界以下の濃度であるので、安全に操作を実施することができる。

【００９３】このような４％以下の微量のH_2 を含むN_2 ガスの供給は、アノード２の電位を低減し、かつ、カソード３の電位を電圧値として観測可能にする。すなわち、燃料電池保管中において電池内に大気中から混入した酸素に起因してアノード２が高電位状態（０．８Ｖ以上）にある場合でも、供給されたH_2 がアノード２の触媒に吸着するので、アノード２は、H_2 電位である０Ｖ付近まで低減する。一方、同様にカソード３は高電位状態にあるため、アノード２の電位が低下したことで、アノード２とカソード３の間に電圧が発生する。電圧検出器２０は、この発生電圧を検知し、検出値を制御装置２６に送信し続ける。

【００９４】そして、発生電圧が予め設定された所定の電圧抑制開始電圧値、例えば０．７Ｖ／セル以上に到達した場合、制御装置２６は、ダミー抵抗開閉器１９に投入信号を与えてダミー抵抗１７を投入し、カソード３中の混入O_2 を消費することで、電圧を低減させ、カソード３電極電位の抑制を行う。

【００９５】（効果）以上のような本実施の形態によれば、前記第２の実施の形態の効果に加えて、さらに以下のような効果が得られる。すなわち、昇温操作において、燃料電池保管中に電池電池内に大気中から混入した酸素により発生する高電位状態（０．８Ｖ以上）の電極を、触媒劣化が進行する１００℃以上の高温状態に到達する前に、アノード２に４％以下の微量のH_2 を供給することにより、アノード電位を低減し、かつ、ダミー抵抗１７を投入してカソード３中のO_2 を消費することで、カソード電位を抑制することができる。したがって、昇温に伴う高温、高電位状態で進行する触媒劣化を完全に防止できる。

【００９６】（６）第６の実施の形態

請求項１０、１５記載の発明を適用した一つの実施の形態を、第６の実施の形態として図５を参照して以下に説明する。

【００９７】（構成）まず、本実施の形態に用いる燃料電池発電プラントの構成は、図１に示した前記第１の実施の形態において、さらに、カソード３側に微量の空気を混入するための構成を追加したものである。すなわち、カソード３の入口に配置してあるカソードN_2 供給弁１４の上流には、カソード空気混入調整弁３０を介して、カソード空気供給系統３１が接続されている。ここで、カソード空気混入調整弁３０は、カソードN_2 供給弁１４が開操作してカソード３にN_2 が供給される場合に、このカソードN_2 供給弁１４と同時にカソード空気混入調整弁３０が開操作するように構成されている。さらに、この開操作におけるカソード空気混入調整弁３０の弁開度は、カソード３に供給されるN_2 ガス中のO_2 濃度が０．００５～０．０５％を満足するように調整され、その制御は制御装置２６により実施されるようになっている。なお、他の部分については、前記第１の実施の形態と全く同様に構成されている。

【００９８】（作用）以上のような構成を有する本実施の形態の作用は以下の通りである。すなわち、停止指令が入力された場合、発電運転状態から停止状態への移行に伴い、制御装置２６は、所内電力相当の最低負荷まで負荷低減操作を指令する。最低負荷レベル到達後、制御装置２６は、外部負荷系統開閉器２４に開信号を与えて外部負荷系統２２を切り離し、かつ所内電力系統開閉器２３には閉信号を保持し、所内電力系統２１だけの最低負荷レベルによるアイドルモード運転を継続する。

【００９９】また、制御装置２６は、停止指令と同時に電池冷却水系統４に降温信号を与え、アイドルモード運転と並行して燃料電池本体１の降温操作を実施する。この場合、温度センサ２５は、アイドルモード運転中の燃

料電池本体１のホットスポットを連続的に検出し、検出値を制御装置２６に送信し続ける。

【０１００】そして、温度センサ２５からの検出値が、１５０～１８０℃の範囲、望ましくは１５０℃に到達した段階で、制御装置２６は、所内電力系統開閉器２３およびインバータ開閉器１８に開信号を与え、燃料電池負荷遮断を実施すると同時に、燃料供給遮断弁７および空気供給遮断弁１１に全閉信号を与えて燃料および空気の供給を遮断する。制御装置２６は、この反応ガス供給遮断制御に並行してさらに、不活性ガス供給制御機能によってアノード入口およびカソード入口のN_2 供給弁１０，１４に開信号を与えて、アノード２およびカソード３に対し、N_2 によるガス置換操作を実施する。

【０１０１】この時、アノード２の残留H_2 リッチガスおよびカソード３の残留空気により残留電圧が発生するが、この残留電圧は電圧検出器２０によって検出されて制御装置２６に送信され、電池電圧の抑制制御が実施される。すなわち、制御装置２６は、電圧検出器２０からの検出値が所定値を越えた場合、例えば０．８Ｖ／セルを越えた場合に、ダミー抵抗開閉器１９に投入信号を与えて、ダミー抵抗１７による回路を形成し、電池出力を消費することで、電池電圧の抑制を実施する。

【０１０２】さらに、本実施の形態において、以上のようにカソードN_2 供給弁１４を開操作してカソード３にN_2 を供給する際に、制御装置２６は、カソードN_2 供給弁１４と同時にカソード空気混入調整弁３０も開操作し、その弁開度を制御するため、カソード空気供給系統３１からカソード３に０．００５～０．０５％のO_2を含むN_2 が供給される。このように、０．００５～０．０５％の濃度のO_2 が供給されることにより、カソード３の電極電位は、０．３～０．８Ｖの範囲を確実に維持する。

【０１０３】以上の操作により、燃料電池本体１自身の発電停止操作が完了するが、制御装置２６は、電池保管温度まで、燃料電池本体１の降温操作を継続する。

【０１０４】（効果）以上のような本実施の形態によれば、前記第１の実施の形態の効果に加えて、さらに以下のような効果が得られる。すなわち、停止操作に伴う不活性ガスによるガス置換操作が実施された状態で、不活性ガス中に微量の酸素が含まれているので、電極電位はその微量酸素に平衡となる電位状態に維持される。

【０１０５】図６は、本発明者等が実験により求めたO_2 濃度と電極電位の関係を示すものである。図６に示すように、触媒組成によりO_2 濃度と電極電位の関係は変化する（これは、触媒組成である貴金属とカーボンとの混成電位で決定するものである）。一方、前述したように、図８は、停止操作後の電極電位と、その停止操作に伴う電圧低下量の関係を示している。

【０１０６】これらの図６と図８のグラフより、酸素濃度０．００１～０．１％における電極電位は、おおよそ、種々の触媒組成においても０．３～０．８Ｖを示し、この電位範囲は、停止操作に伴う電圧低下を抑制できることが明らかである。つまり、電極電位が０．８Ｖを越える場合には、触媒のシンタリングが加速するため、停止操作に伴う電圧低下を引き起こし、一方、電極電位が０．３Ｖ以下の場合には、シンタリングにより溶解した触媒貴金属が再析出して触媒の活性サイトを覆うために触媒活性面積が減少し、停止操作に伴う電圧低下を引き起こすものと考えられる。

【０１０７】したがって、発電停止後においても不活性ガス中の酸素濃度が０．００１～０．１％であることにより、電極電位を０．３～０．８Ｖに保持することができ、上述したような触媒劣化現象を回避することができる。特に、本実施の形態のように、酸素濃度を０．００５～０．０５％に限定した場合には、図６から明らかなように、触媒組成に関わらず、電極電位を確実に０．３～０．８Ｖに保持できる。

【０１０８】なお、本実施の形態は、カソード３のパージ用N_2 中に微量のO_2 を混入させるものであるが、同様に、アノード２のパージ用N_2 に微量のO_2 を混入させることにより、アノード触媒に関して同様な効果を得ることができる。なお、アノード２とカソード３のどちらか一方のパージ用N_2 に微量のO_2 を混入させた場合には、アノード２とカソード３間にある電解質層をO_2が溶解、拡散移動するため、若干の時間遅れ（１０ｍｉｎ程度）が生じるものの、両極とも微量のO_2に平衡する電極電位を保持することができる。

【０１０９】（７）他の実施の形態

本発明は、以上のような実施の形態に限定されるものではない。例えば、前述したように、個々の実施の形態は明らかな効果を有するが、前記の複数の実施の形態を適宜組み合わせることにより、相乗的な効果を得ることが可能である。また、制御装置や供給弁、供給系統等の各部の具体的な構成は適宜選択可能である。

【０１１０】

【発明の効果】以上説明したように、本発明によれば、所内電力系統だけのアイドルモード運転を実施したり、ガス置換用の不活性ガス中に微量水素や微量酸素を含有させることにより、燃料電池本体の電圧を十分に抑制できるため、起動操作時や停止操作時における触媒の劣化を防止して、起動停止操作に伴う電池特性を低下させることなく安定に維持することが可能な、優れた燃料電池発電プラントおよびその起動・停止方法を提供することができる。

【図面の簡単な説明】

【図１】本発明による第１および第３の実施の形態に係る燃料電池発電プラントを示す接続構成図。

【図２】燃料電池触媒のシンタリングに伴う触媒表面減少比と触媒温度の関係を示すグラフ。

【図３】本発明による第２および第４の実施の形態に係

る燃料電池発電プラントを示す接続構成図。

【図4】本発明による第5の実施の形態に係る燃料電池発電プラントを示す接続構成図。

【図5】本発明による第6の実施の形態に係る燃料電池発電プラントを示す接続構成図。

【図6】O_2 濃度と電極電位の関係を示すグラフ。

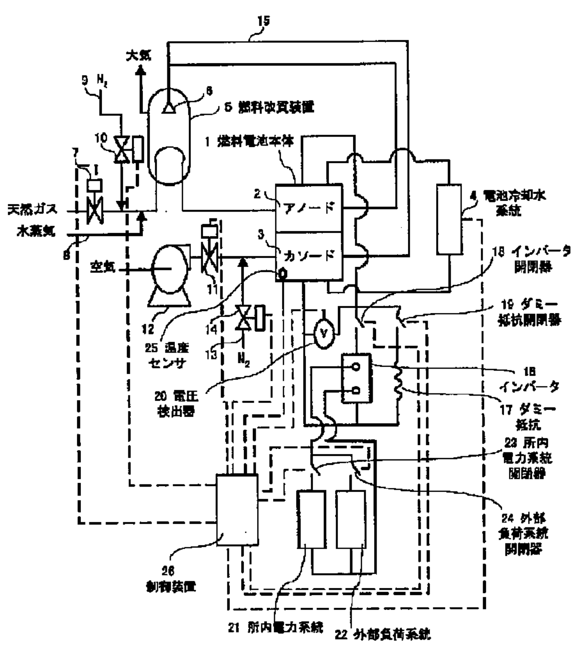
【図7】従来のリン酸型燃料電池発電プラントの一例を示す接続構成図。

【図8】起動停止操作中の電極電位と起動停止操作に伴う電圧低下量の関係を示すグラフ。

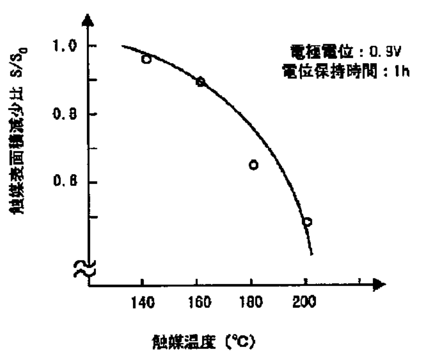
【符号の説明】

1…燃料電池本体
2…アノード
3…カソード
4…電池冷却水系統
5…燃料改質装置
6…改質器バーナ
7…燃料供給遮断弁
8…水蒸気供給経路
9…アノードN_2 供給系統
10…アノードN_2 供給弁
11…空気供給遮断弁
12…ブロワ
13…カソードN_2 供給系統
14…カソードN_2 供給弁
15…ガス排気経路
16…インバータ
17…ダミー抵抗
18…インバータ開閉器
19…ダミー抵抗開閉器
20…電圧検出器
21…所内電力系統
22…外部負荷系統
23…所内電力系統開閉器
24…外部負荷系統開閉器
25，27…温度センサ
26…制御装置
28…微量H_2 含有N_2 供給弁
29…微量H_2 含有N_2 供給系統
30…カソード空気混入調整弁
31…カソード空気供給系統

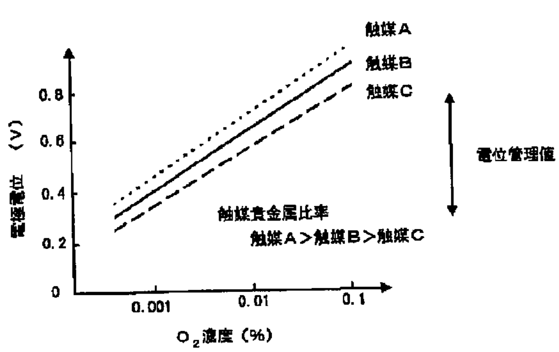
【図1】



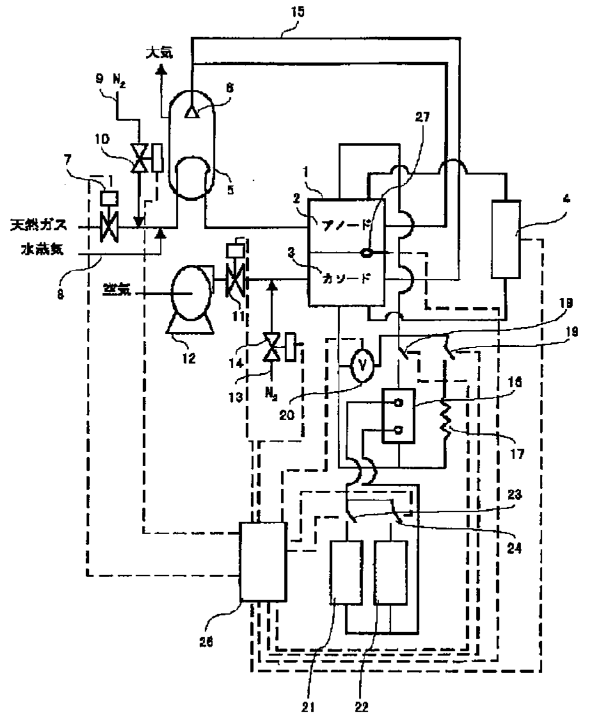
【図2】



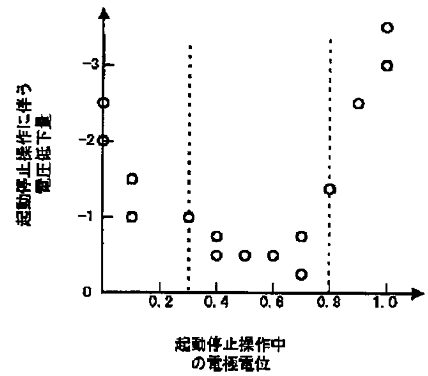
【図6】



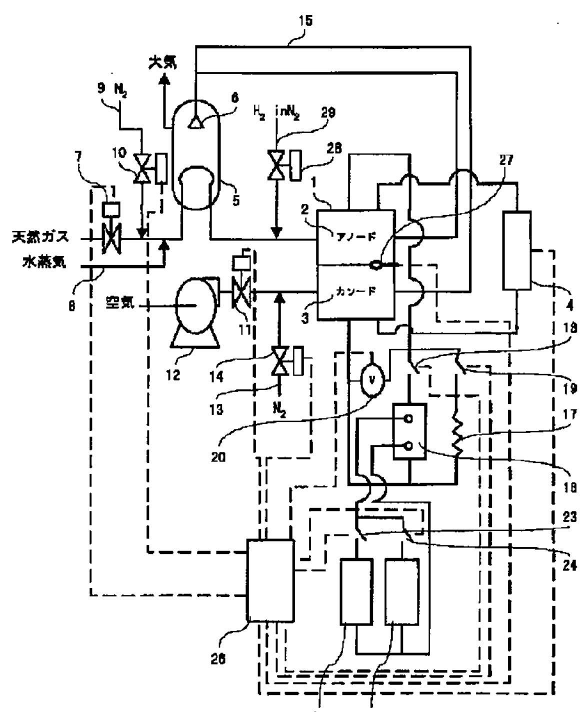
【図３】


15
大気
9 N_2
6
10
27
7
1
2
5
4
天然ガス
水蒸気
アノード
3
カソード
8
空気
11
12
14
13
N_2
20
19
16
17
23
24
26
21
22

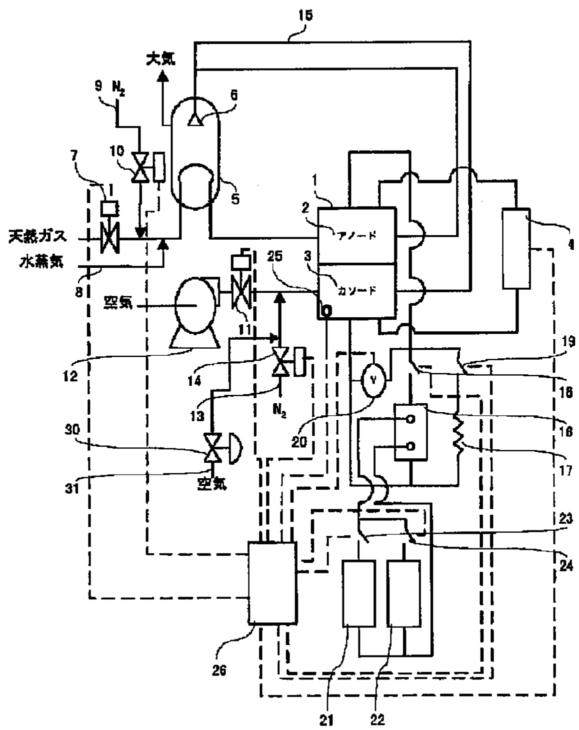
【図８】


起動停止操作に伴う電圧低下量
-3
-2
-1
0
0.2
0.4
0.6
0.8
1.0
起動停止操作中の電極電位

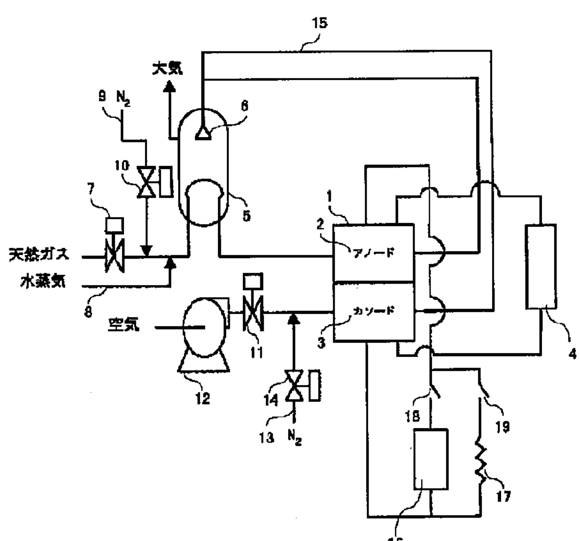
【図４】


15
大気
9 N_2
6
H_2 inN_2
29
28
10
7
1
2
5
27
天然ガス
水蒸気
アノード
8
空気
カソード
3
11
4
12
14
13
N_2
18
19
17
20
16
23
24
26
21
22

【図５】


15
大気
9 N_2
6
10
7
5
1
2
アノード
天然ガス
水蒸気
25
3
カソード
4
8
空気
11
12
14
19
13
N_2
18
V
20
16
30
17
31
空気
23
24
26
21
22

【図７】


15
大気
9 N_2
6
10
7
5
1
2
アノード
天然ガス
水蒸気
8
空気
カソード
11
3
4
12
14
18
19
13
N_2
17
16